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PART I
SYNTHETIC HIGH PERFORMANCE FLUIDS: CHEMISTRY, TECHNOLOGY, AND COMMERCIAL IMPORTANCE

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Poly(α-olefins)

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I. INTRODUCTION

Saturated olefin oligomers are a class of synthetic high performance functional fluids that have been developed to meet the increasingly stringent demands being placed on today's working fluids. The term poly(α-olefin), or PAO, is commonly used to designate such fluids, and that designation is used in this chapter. The term PAO was first used by Gulf Oil Company (later acquired by Chevron), but it has now become an accepted generic appellation for hydrocarbons manufactured by the catalytic oligomerization (polymerization to low molecular weight products) of linear olefins having six or more (usually ten) carbon atoms [1].

Technological advances are often accompanied by a variety of unanticipated problems and complications. Advances in the function and efficient operation of modern machines and engines have brought new challenges relating to the satisfactory use and performance of existing functional fluids. Among these challenges are:

operation under increasingly severe conditions
the need for more cost-effective, hence more competitive, operations
the need to lessen dependence on the availability of crude oil stocks
the specialized performance requirements of emerging end-use applications
the necessity of accounting for the critically important, but long-ignored, toxicological and biodegradable characteristics of the fluids being used

Today, mineral oil base stocks are being refined to give products that are certainly superior to those available only a few years ago. But the limits to which mineral oils can be economically refined are being strained. To satisfactorily address the challenge of solving the problems noted above, industry is turning to synthetic alternatives.

PAOs are gaining rapid acceptance as high performance lubricants and functional fluids

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because they exhibit certain inherent, and highly desirable, characteristics [1]. Among these favorable properties are:

a wide operational temperature range
good viscometrics (high viscosity index) thermal stability
oxidative stability
hydrolytic stability
shear stability
low corrosivity
compatibility with mineral oils
compatibility with various materials of construction low toxicity
manufacturing flexibility that allows "tailoring" products to specific end-use application requirements

II. HISTORICAL DEVELOPMENT

A. Technical

Synthetic oils consisting only of hydrocarbon molecules were first produced by the prominent chemists Charles Friedel and James Mason Crafts in 1877 [2]. Standard Oil Company of Indiana attempted to commercialize a synthetic hydrocarbon oil in 1929 but was unsuccessful because of a lack of demand. In 1931 Standard Oil, in a paper by Sullivan et al., disclosed a process for the polymerization of olefins to form liquid products [3]. These workers employed cationic polymerization catalysts such as aluminum chloride to polymerize olefin mixtures obtained from the thermal cracking of wax. At about the same time that the work at Standard Oil was being carried out, H. Zorn of I.G. Farben Industries independently discovered the same process [4].

The first use of a linear α-olefin to synthesize an oil was disclosed by Montgomery et al. in a patent issued to Gulf Oil Company in 1951 [5]. Aluminum chloride was used in these experiments, as in the earlier work with olefins from cracked wax.

The use of free radical initiators as α-olefin oligomerization catalysts was first patented by Garwood of Socony-Mobil in 1960 [6]. Coordination complex catalysts, such as the ethylaluminum sesquichloride/titanium tetrachloride system, were disclosed in a patent issued to Southern et al. at Shell Research in 1961 [7].

The fluids produced by the various catalyst systems described above contained oligomers with a wide range of molecular weights. The compositions and internal structures of these fluids resulted in viscosity–temperature characteristics that gave them no particular advantage over the readily available and significantly less expensive mineral oils of the day.

In 1968 Brennan at Mobil Oil patented a process for the oligomerization of α-olefins using a BF_3 catalyst system [8]. Prior to that time, BF_3 catalysis had given irreproducible results. Brennan showed that the reaction could be controlled if two streams of olefins were mixed in the reactor. The first stream contained the olefin plus a $BF_3 \cdot ROH$ complex, where ROH is an alcohol. The second stream contained the olefin saturated with gaseous BF_3. Of particular interest, this catalyst system produced a product consisting of a mixture of oligomers that was markedly peaked at the trimer.

Shubkin of Ethyl Corporation showed that H_20 [9], as well as other protic cocatalysts such as alcohols and carboxylic acids [10], could be used in conjunction with BF_3 to produce oligomers of uniform quality. The experimental technique employed a molar excess of BF_3 in relation to the cocatalyst. The excess was achieved by sparging the reaction medium with BF_3 gas

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throughout the course of the reaction or by conducting the reaction under a slight pressure of BF_3. These studies showed that the oligomerization products exhibited pour points that were well below those anticipated for such compounds, even when dimeric products were allowed to remain in the final mixture. The molecular structure of the dimer was believed to consist of a straight carbon chain containing a single methyl group near the middle. Such branched structures were known to exhibit relatively high pour points. More pertinent to the current subject, these were the first patents to address the potential importance of PAOs derived from $BF_3 \cdot ROH$ catalyst systems as synthetic lubricants. Shubkin et al. later showed that the unique low temperature properties could be attributed to a high degree of branching in the molecular structure [11].

B. Commercial

The commercial development of PAO fluids as lubricants and high performance functional fluids began in the early 1970s, but significant growth in markets and in the variety of end-use applications did not begin until the latter part of the 1980s. During this time, several companies played significant roles with both R&D and market development efforts [12].

1. Amsoil Corporation

Amsoil Corporation was apparently the first company to market a full synthetic lubricant certified by the American Petroleum Institute (API). However, this product, which was introduced in 1972, was 100% diester based. It was not until late 1977 that Amsoil introduced a full synthetic 10W-40 motor oil based on PAO/ester [13]. Amsoil has also introduced a semisynthetic diesel engine oil, a full synthetic gear oil based on PAO/ester and PAO-based greases. In 1996 the firm introduced a PAO/ester-based 0W-30 motor oil.

2. Mobil Oil Corporation

Mobil Oil Corporation was the first company to introduce a PAO-based synthetic lubricant. In 1973 Mobil began marketing a synthetic motor oil for use in automotive engines in overseas markets. Circulating oils and gear oils were added to the Mobil line in 1974. The first U.S. test marketing of Mobil 1 Synthesized Engine Lubricant began in the autumn of 1974. The test was expanded to eight cities in September 1975, and to all Mobil marketing areas in April 1976. Mobil 1 was initially an SAE 5W-20 product, but it was later replaced by a 5W-30 fluid based on PAO and a neopentyl polyol ester. The polyol ester improved additive solubility and increased seal swell.

Mobil's product distribution was extended to Canada, Japan, and several European countries in 1977. Also in 1977, Mobil introduced Delvac 1, a PAO-based product aimed at the truck fleet market. Mobil also pioneered PAO-based industrial lubricants with its line of Mobil SHC products.

Mobil's PAO plant in the United States has an estimated annual capacity of 52,000 metric tons. A new plant at Notre Dame de Gravenchon, France, reportedly has an annual capacity of 50,000 metric tons. Mobil purchases 1-octene, 1-decene, and 1-dodecene for its PAO production.

In addition to the low viscosity PAOs, Mobil produces two grades of high viscosity PAO. The annual sales for these products are believed to be around 4000 metric tons.

3. Gulf Oil Company

Gulf Oil Company appears to have had an interest in synthetic hydrocarbons in the 1940s. Developmental work at the Gulf laboratories in Harmarville, Pennsylvania, continued into the 1960s and 1970s. In 1974 Gulf built a semiworks plant with a capacity of 1125 metric tons per year. The first commercial sale from this plant was in December 1974.

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During the years 1976–1980, Gulf introduced an arctic super-duty 5W-20 CD/SE crankcase lubricant plus an arctic universal oil/transmission oil. In Canada, Gulf began marketing PAO-based gear lubricants, synthetic greases, and a partial synthetic 5W-30 crankcase oil.

In December 1980 Gulf began commercial production in their PAO plant in Cedar Bayou, Texas, strategically located next to Gulf's olefin plant. The initial production capacity was 15,400 metric tons per year. In 1981–1983 Gulf added several new PAO-based products to their line of synthetic fluids. These included Gulf Super Duty II, a full synthetic 0W-30 crankcase oil, Gulf SL-H, a hydraulic fluid for high and low temperature operation, and Gulf Syngear, a 75W-90 gear oil for long life and fuel economy. In addition to their fully formulated products, Gulf marketed PAO to the merchant market under the trade name Synfluid Synthetic Fluids. Gulf Oil Corporation was acquired by Chevron Corporation in 1984.

4. Chevron Corporation

Prior to 1984, Chevron marketed a single synlube-based product. That product was Chevron Sub Zero Fluid, a 7.5W-20 CD/SE crankcase oil for use in construction equipment and vehicles employed in the Alyeska Pipeline Project in Alaska. In June 1984 Chevron acquired Gulf Oil Company. In late 1985 the PAO manufacturing and marketing responsibilities were transferred to the Oronite Division of Chevron Chemical. Chevron continued to offer the PAO-based arctic oil plus Chevron Tegra PAO-based synthetic lubricants, which included the old Gulf Syngear and three grades of compressor oils. Unlike Mobil, which chose to market aggressively under their own name, Chevron decided to focus on the merchant market. The capacity of the Chevron plant has been increased to approximately 24,000 metric tons. Chevron, like Amoco Corporation, but unlike Mobil, is basic in the α-olefin raw material used to manufacture PAO fluids.

5. Amoco

Amoco, formerly Standard Oil Company (Indiana), was probably the first U.S. petroleum company to investigate synthetic hydrocarbon fluids. The pioneering work by F.W. Sullivan in the early 1930s was mentioned above [3]. Those efforts led to a patent mat described the aluminum chloride catalyzed polymerization of olefins derived from cracked wax [14]. An attempt to commercialize a synthetic lubricating fluid in 1929 was abandoned because of lack of demand.

In 1982 Amoco Oil Company began test marketing a 100% PAO-based lubricant. This venture was followed in April 1984 by the introduction of Amoco's Ultimate line of crankcase oils for both gasoline and diesel oils. Amoco later expanded the product line to include gear oils and grease bases. All the PAO for the Ultimate products were purchased until 1996, when Amoco purchased both the α-olefin and PAO technology plants from Albemarle Corporation. Amoco currently has the technology and resources to produce PAOs directly from its own ethylene.

6. Ethyl Corporation

In 1970 Ethyl began conducting research on a process for the polymerization of linear α-olefins to form low viscosity functional fluids. The concept was attractive because Ethyl was one of the world's largest manufacturers of linear α-olefins. The target application was a hydraulic fluid specification for military jet aircraft. As it turned out, the specifications were written around an experimental fluid from Mobil, and the independent research at Ethyl led to a similar BF_3-catalyzed process and decene-based product as that developed by Mobil.

Ethyl chose not to commercialize its findings because the potential market at that time was small. Following the oil embargo of 1974, and the subsequent introduction of Mobil 1, Ethyl reinstituted a PAO research program. Ethyl entered the merchant market for PAO base fluids in the late 1970s through a toll manufacturing arrangement with Bray Oil in California. In 1981

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Ethyl decided to build a market development unit (MDU) to manufacture PAO in Baton Rouge, Louisiana. The 7000 metric ton MDU came onstream in mid-1982, and Ethyl intended this plant to operate until the market had grown to a size that would justify a world-scale plant. Marketing of the PAO was handled by Ethyl's Edwin Cooper Division, which was responsible for the manufacture and marketing of Ethyl's lube oil additives, and the division trade name HiTEC was used for the fluids. The division name was later changed to Ethyl Petroleum Additives Division (EPAD).

Slow growth in the PAO market prompted Ethyl to shut down the MDU in 1985 and return to a toll arrangement. In 1987 Ethyl entered into an agreement with Quantum Chemical whereby Quantum would manufacture PAO from Ethyl's decene. Ethyl's PAO sales in Europe began to grow rapidly, and a decision was made to build a plant at Ethyl's manufacturing site at Feluy, Belgium, where a large new α-olefin plant was also being planned.

In early 1989 Ethyl transferred responsibility for the PAO project from the Ethyl Petroleum Additives Division to the Industrial Chemicals Division. This decision reflected the philosophy that PAO is a base stock rather than a lube additive, and the action allowed Ethyl to expand the scope of the sales effort to include a broader potential market. In keeping with the philosophy of PAO being a base stock, the trade name for the bulk fluids was changed to ETHYLFLO PAO fluids, and an aggressive marketing campaign in North America was launched.

In 1989 Quantum sold its Emery Division to Henkel, but retained its PAO plant at Deer Park, Texas, leaving Quantum in the difficult situation of having neither its own source of 1-decene nor its own marketing organization. In 1990 Ethyl purchased Quantum's Deer Park plant, which is located only a few miles from Ethyl's large α-olefin plant at Pasadena. The Deer Park facility has two PAO production trains and an annual capacity of 77,000 metric tons. Ethyl's 36,000 metric ton Feluy plant came onstream in January 1991. Ethyl in 1994 split off Albemarle as a separate company, which owned and operated the PAO business, but in March 1996 Amoco purchased the α-olefin and PAO business from Albemarle. Albemarle marketed PAO under the DURASYN PAO trade name.

7. Exxon Corporation

Exxon introduced Esso Ultra Oil in Europe in mid-1986. This lubricant is a partial synthetic oil containing PAO. Exxon has produced small quantities of PAO in its alkylation facility at its chemical plant in Port Jerome, France. Plans to convert that plant to full-scale PAO operation appear to have been shelved.

8. Quantum Chemical Corporation

Quantum Chemical Corporation is the name adopted in 1988 by the former National Distillers and Chemical Corporation. National Distillers entered the synthetic lubricants business in 1978 with the purchase of Emery Industries, an important producer of ester-based synlubes.

In December 1980 National Distillers announced the construction of a 15,400 metric ton PAO plant at their manufacturing facility in Deer Park, Texas. The plant did not actually come onstream until late 1983. In 1987 National Distillers entered into a manufacturing and marketing agreement with Ethyl Corporation, as described above. The 1-decene feedstock was supplied by Ethyl.

By 1989, Quantum had debottlenecked the PAO plant and built a second, larger plant at the same location, bringing the total capacity to 77,000 metric tons. In 1990 Quantum sold their PAO business and manufacturing site to Ethyl Corporation. In 1994 Ethyl spun off Albemarle Corporation. The PAO business and manufacturing site became part of Albemarle Corporation, but, as mentioned above, was sold to Amoco in March 1996.

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9. Castrol Limited

Castrol, originally the Burmah Oil Public Limited Company, and then Burmah-Castrol, has historically been an innovator in automotive lubricant marketing. In 1981 Castrol purchased Bray Oil Company, a small manufacturer of synthetic lubricants based in California. Bray Oil at that time had been toll-producing PAO for Ethyl Corporation. Although Castrol maintained a strong interest in marketing synthetic lubricants, they chose to close the PAO plant and purchase their PAO requirements.

Castrol was an early marketer of synthetic automotive lubricants in Europe. They have introduced a full line of synthetic and semisynthetic gear lubes and compressor oils as well as higher performance jet turbine oils, military hydraulic fluids and jet lube products. They introduced Syntron X—a 5W-50 PAO-based automotive synlube—into the United Kingdom in 1988, and a new line of PAO-based automotive products, under the trade names Syntorque and Transmax, was introduced into the United States in 1991. Castrol introduced a 5W-50, Syntec PCMO in 1993 followed by a 10W-30 oil. They also introduced Syntec Blend, a part synthetic, in late 1995.

10. Uniroyal Chemical Company

Since 1980, Uniroyal has produced high viscosity PAOs (kinematic viscosities at 100°C of 40 and 100 cSt) in a small plant at Elmira, Ontario. Uniroyal and Mobil are the only producers of these grades of PAO in the world. Total production capacity is about 2000 metric tons per year.

11. Neste Chemical

Neste Chemical has a PAO plant in Beringen, Belgium. The facility came onstream in 1991 and was estimated to have a capacity of 28,000 metric tons. Current production is estimated to be 35,000 tons per year.

12. Texaco

Texaco has conducted research on PAOs and holds several patents but has no commercial production. They do, however, market PAO-based lubricants under the trade name Havoline.

13. Shell Chemical

Shell Chemical has conducted extensive research on PAOs but has never begun commercial manufacturing. Shell, along with Chevron and Amoco, is basic in the α-olefin raw material.

14. Idemitsu Petrochemicals

PAOs are not currently produced in Japan. However, Idemitsu Petrochemicals raised interest in plant construction several years ago. To date, they have not announced plans to build a PAO plant on their own or with another company.

15. Sasol

In South Africa Sasol produces 1.4 million metric tons/year of mixed α-olefins from its coal to hydrocarbons process via Fischer–Tropsch chemistry. Sasol is considering plans to produce PAOs and oxo alcohols in the future [15].

Sasol has announced plans recently to double its α-olefins capacity at its coal to synthetic fluids facility in South Africa [16]. By fourth quarter of 1997, Sasol will have a capacity of 110,000 metric ton per year of hexane with further expansion planned in 1998–1999, which is expected to include pentene capacity.

Sasol is expected to spend $50 million to build a 50,000 metric ton/year 1-octene unit at the facility. This unit is expected to be onstream by 1999.

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III. CHEMISTRY

PAOs are manufactured by a two-step reaction sequence from linear α-olefins, which are derived from ethylene. The first step is synthesis of a mixture of oligomers, which are polymers of relatively low molecular weight.

$$\alpha\text{-olefin} \rightarrow \text{dimer} + \text{trimer} + \text{tetramer} + \text{pentamer, etc.}$$

For the production of low viscosity PAOs (2–10 cSt), the catalyst for the oligomerization reaction is usually boron trifluoride. (PAOs are commonly classified according to their approximate kinematic viscosity at 100°C—this convention is used throughout this chapter.) The BF_3 catalyst is used in conjunction with a protic cocatalyst such as water, an alcohol, or a weak carboxylic acid. It is necessary that the BF_3, a gas, be maintained in a molar excess relative to the protic cocatalyst. Although this stoichiometry may be accomplished by sparging the reaction mixture with a stream of BF_3, it is more practical, on a commercial basis, to conduct the reaction under a slight BF_3 pressure (10–50 psig). For convenience, a general designation for the catalyst system is $BF_3 \cdot ROH$, where ROH represents any protic species such as those noted above, and the presence of excess BF_3 is understood.

The $BF_3 \cdot ROH$ catalyst system is unique for two reasons. First, this catalyst combination produces an oligomer distribution that is markedly peaked at trimer. Figure 1 shows a gas chromatography (GC) trace indicating the oligomer distribution of a typical reaction product derived from 1-decene using a $BF_3 \cdot n\text{-}C_4H_9OH$ catalyst combination at a reaction temperature of 30°C. The chromatogram indicates that only a relatively small amount of dimer is formed. The bulk of the product is the trimer, with much smaller amounts of higher oligomers present.

The second unique feature of the $BF_3 \cdot ROH$ catalyst system is that it produces products that have exceptionally good low temperature properties. The extremely low pour point values puzzled the early workers in the field until it was shown that the resulting oligomers exhibit a greater degree of skeletal branching than would be predicted by a conventional cationic polymerization mechanism [11].

The reason that BF_3 catalysis causes excess skeletal branching during the oligomerization process is unclear. The first researcher to recognize the phenomenon proposed a mechanism involving a skeletal rearrangement of the dimer [11]. A later paper proposed that the monomer undergoes rearrangement [17]. A third paper proposed that the excess branching arises from positional isomerization of the double bond in the monomer prior to oligomerization [18]. In

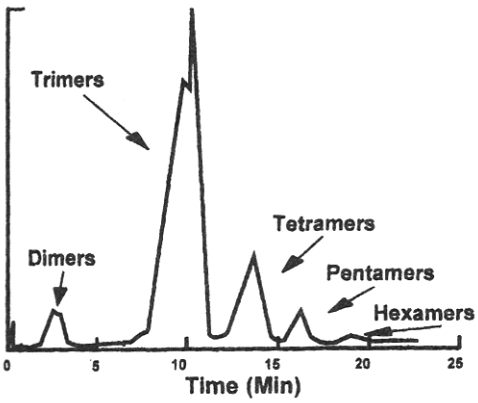

Figure 1 Gas chromatography of typical oligomer.

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fact, the large number of isomers that are formed cannot be explained by any single mechanism, and the role of $BF_3 \cdot ROH$ in promoting the necessary rearrangements remains unexplained.

Even though the mechanism of the BF, · ROH-catalyzed oligomerization remains to be fully elucidated, researchers have learned how to advantageously control the composition of the final PAO product to permit the tailoring of the oligomer distribution to fit the requirements of specialized end-use applications [19]. This customizing is done by manipulation of the reaction variables, which include:

chain length of olefin raw material
temperature
time
pressure
catalyst concentration
cocatalyst type and concentration
cocatalyst feed rate
olefin feed rate
reaction quench and recovery procedures
hydrogenation catalyst and conditions
distillation

In addition to controlling the relative distribution of the oligomers by manipulation of the reaction parameters, the PAO manufacturer can make major alterations in the product properties by choice of starting olefin. Today, the commercial PAO market is dominated by decene-derived materials because these products have the broadest range of properties, but a knowledgeable producer has the option of choosing other starting olefins to better satisfy the requirements for a particular end-use application. For example, PAO based on C_{12}-olefin is manufactured commercially by Chevron and Mobil. Mobil also makes PAO materials containing oligomers based on 1-octene, 1-decene, and 1-dodecene mixtures. More detail on the potential use of alternate olefin streams is provided later.

The crude reaction product is quenched with water or caustic, allowed to settle, and then washed again with more water to remove all traces of the BF_3 catalyst. Gaseous BF_3 can be recovered by concentrating the wash water and treating the solution with concentrated sulfuric acid.

A second step in the manufacturing process entails hydrogenation of the unsaturated oligomer. The hydrogenation may be carried out before or after distillation. Distillation is required to remove any unreacted monomer, to separate the dimer, which is marketed as a 2.0 cSt product, and in some cases to coproduce a lighter and a heavier grade of PAO.

The hydrogenation is typically performed over a supported metal catalyst such as nickel/kieselguhr or palladium/alumina. Hydrogenation is necessary to give the final product enhanced chemical inertness and added oxidative stability. The term poly(α-olefin) is used even though the fluid is saturated in a subsequent chemical hydrogenation.

It is normally not possible to manufacture the higher viscosity PAO products (40 and 100 cSt) using the $BF_3 \cdot ROH$ technology. However, several other catalyst systems are known that can give the desired products. One class of catalysts employs alkylaluminum compounds in conjunction with $TiCl_4$ [7] or alkyl halides [20]. The latter system is preferred by Uniroyal, which uses ethylaluminum sesquichloride with allyl chloride.

It has also been reported in a Mobil Oil European patent application that high viscosity PAOs may be produced by dimerizing lower oligomers with peroxides [21]. The patent describes the use of stoichiometric quantities of di-*tert*-butyl peroxide, which probably would not be economically feasible. On the other hand, a system that employs hydrogen peroxide directly or the

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regeneration of an active intermediate might be commercially attractive. Mobil has also obtained a large number of patents describing the use of supported chromium catalysts [22]. The system actually employed by Mobil for commercial manufacture has not been disclosed, but it is believed to employ an aluminum chloride catalyst.

IV. PROPERTIES

The physical and chemical properties of PAO fluids make them attractive for a variety of applications requiring a wider temperature operating range than can normally be achieved by petroleum-based products (mineral oils). An excellent review of poly(α-olefin)-based fluids as high performance lubricants has recently been published [23]. The chapter appendix presents tabular summaries of the properties of commercially available PAOs.

A. Physical Properties

1. Commercial PAOs

Table 1 lists the typical physical properties of the five grades of commercial low viscosity PAOs available today. These products are all manufactured using 1-decene as the starting material, and the final properties are determined by control of the reaction parameters and (depending on the manufacturer) selective distillation of the light oligomers.

Table 1 shows that all commercial grades of low viscosity PAOs have relatively high viscosity indexes (VIs) of around 135. [*Note:* No VI is shown for PAO 2 because VI is undefined for fluids having a kinematic viscosity (KV) of less than 2.0 cSt at 100°C.] The viscosity of a high VI fluid changes less dramatically with changes in temperature compared to the viscosity changes of a low VI fluid. A practical consequence of this property is that PAOs do not require viscosity index improvers (VIIs) in many applications. The presence of a VII is often undesirable because many of these agents tend to be unstable toward shear. Once the VII begins to break down, the fully formulated fluid goes "out of grade" (i.e., fails to retain the original viscosity grade).

Several other important physical properties of commercial PAOs are shown on Table 1. All the products have extremely low pour points as well as low viscosities at low temperatures. These properties make PAOs very attractive in the cold-climate applications for which they were first used. At the other end of the spectrum, all but the 2.0 cSt product have low volatilities, as demonstrated by the low percent loss of material at 250°C in the standard NOACK volatility test. Low volatility is important in high temperature operations to reduce the need for "topping up" and to prevent a fluid from losing its lighter components and thus becoming too viscous

Table 1 Physical Properties of Commercial Low Viscosity PAOs

Parameter	Test method	PAO 2	PAO 4	PAO 6	PAO 8	PAO 10
Kinematic viscosity, cSt						
At 100°C	ASTM D-445	1.80	3.84	5.98	7.74	9.87
At 40°C	ASTM D-445	5.54	16.68	30.89	46.30	64.50
At −40°C	ASTM D-445	306	2390	7830	18,200	34,600
Viscosity index		—	124	143	136	137
Pour point, °C	ASTM D-97	−63	−72	−64	−57	−53
Flash point, °C	ASTM D-92	165	213	235	258	270
NOACK, % loss[a]	DIN 51581	99.5	11.8	6.1	3.1	1.8

[a] Volatility at 250°C.

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Table 2 Physical Properties of Commercial High Viscosity PAOs

Parameter	Test method	PAO 40	PAO 100
Kinematic viscosity, cSt			
At 100°C	ASTM D-445	40–42	103–110
At 40°C	ASTM D-445	399–423	1260–1390
At −18°C	ASTM D-445	39,000–41,000	176,000–203,000
Pour point, °C	ASTM D-97	−36 to −45	−21 to −27
Flash point, °C	ASTM D-92	275–280	280–290
NOACK, % loss[a]	DIN 51581	0.8–1.4	0.6–1.1

[a] Volatility at 250°C.

at low or ambient temperatures. Low volatility is also important because it relates to flash and fire points.

The typical physical properties of commercial high viscosity PAO fluids are given in Table 2. The two grades available on the market today are the 40 and 100 cSt fluids. As with the low viscosity PAOs, these fluids have a very broad temperature operating range.

2. Comparison to Mineral Oils

The excellent physical properties of the commercial PAO fluids are most readily apparent when they are compared directly to those of petroleum-based mineral oils. The fairest comparison is to look at fluids with nearly identical kinematic viscosities at 100°C. The differences in both low and high temperature properties can then be examined.

Table 3 compares the physical properties of a commercial 4.0 cSt PAO with those of two 100N (neutral) mineral oils, a 100NLP (low pour) mineral oil, and a hydrotreated VHVI (very high viscosity index) mineral oil. The PAO shows markedly better properties at both high and low temperatures. At high temperatures, the PAO has lower volatility and a higher flash point. A relatively high flash point is, of course, often important for reasons of safety. At the low end of the temperature scale the differences are equally dramatic. The pour point of the PAO is −72°C, while the three 100N mineral oils and the HVI oils are −15, −12, −15, −27°C, −18 and −38, respectively.

Table 3 4.0 cSt Fluids

Parameter	Test method	PAO	100N	100N	100NLP	VHVI	VHVI	VHVI
Base oil group[a]		IV	I	I	I	III	III	III
Kinematic viscosity, cSt								
At 100°C	ASTM D-445	3.84	3.81	4.06	4.02	3.75	4.2	3.98
At 40°C	ASTM D-445	16.7	18.6	20.2	20.1	16.2	—	16.61
At −40°C	ASTM D-445	2390	Solid	Solid	Solid	Solid	NR[b]	NR[b]
Viscosity index		124	89	98	94	121	127	141
Pour point, °C	ASTM D-97	−72	−15	−12	−15	−27	−18	−38
Flash point, °C	ASTM D-92	213	200	212	197	206	210	225
NOACK, % loss[c]	DIN 51581	11.8	37.2	30.0	29.5	22.2	13	13.3

[a] Base stock classification as defined by SAE classification J357.
[b] Not reported.
[c] Volatility at 250°C.

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Table 4 6.0 cSt Fluids

Parameter	Test method	PAO	160HT	240N	200SN	VHVI	VHVI
Base oil group[a]		IV	II	I	I	III	III
Kinematic viscosity, cSt							
At 100°C	ASTM D-445	5.98	5.77	6.98	6.31	5.14	5.9
At 40°C	ASTM D-445	30.9	33.1	47.4	40.8	24.1	
At −40°C	ASTM D-445	7830	Solid	Solid	Solid	Solid	NR[b]
Viscosity index		143	116	103	102	149	127
Pour point, °C	ASTM D-97	−64	−15	−12	−6	−15	−12
Flash point, °C	ASTM D-92	235	220	235	212	230	225
NOACK, % loss[c]	DIN 51581	6.1	16.6	10.3	18.8	8.8	6

[a] Base stock classification as defined by SAE classification J357.
[b] Not reported.
[c] Volatility at 250°C.

Table 4 compares a commercial 6.0 cSt PAO with a 160HT (hydrotreated) mineral oil, a 240N oil, a 200SN (solvent neutral) mineral oil, and VHVI mineral oils that are currently considered to be the best of the mineral oils on the market. The broader temperature range of the PAO is again apparent. Table 5 makes similar comparisons for 8.0 cSt fluids.

The ability of PAO products to outperform petroleum-based products of similar viscosity at both ends of the temperature spectrum becomes easily understandable if one compares the gas chromatography traces. Figure 2 contains chromatograms run under identical conditions of a 4.0 cSt HVI oil and a 4.0 cSt PAO. The PAO product is essentially decene trimer with a small amount of tetramer present. The fine structure of the trimer peak is attributable to the presence of a variety of trimer isomers (same molecular weight, different structure). The HVI oil, on the other hand, has a broad spectrum of different molecular weight products. The oil contains low molecular weight materials that adversely affect the volatility and flash point characteristics. It also contains high molecular weight components that increase the low temperature viscosity and linear paraffins that increase the pour point.

Figure 3 compares the GC traces of a very high quality 6.0 cSt VHVI fluid with a PAO of similar viscosity. The PAO has a well-defined chemical composition consisting of decene trimer, tetramer, pentamer, and a small amount of hexamer. The VHVI fluid, like the HVI fluid

Table 5 8.0 cSt Fluids

Parameter	Test method	PAO	325SN	325N
Base oil group[a]		IV	I	I
Kinematic viscosity, cSt				
At 100°C	ASTM D-445	7.74	8.30	8.20
At 40°C	ASTM D-445	46.3	63.7	58.0
At −40°C	ASTM D-445	18.200	Solid	Solid
Viscosity index		136	99	110
Pour point, °C	ASTM D-97	−57	−12	−12
Flash point, °C	ASTM D-92	258	236	250
NOACK, % loss[b]	DIN 51581	3.1	7.2	5.1

[a] Base stock classification as defined by SAE classification J357.
[b] Volatility at 250°C.

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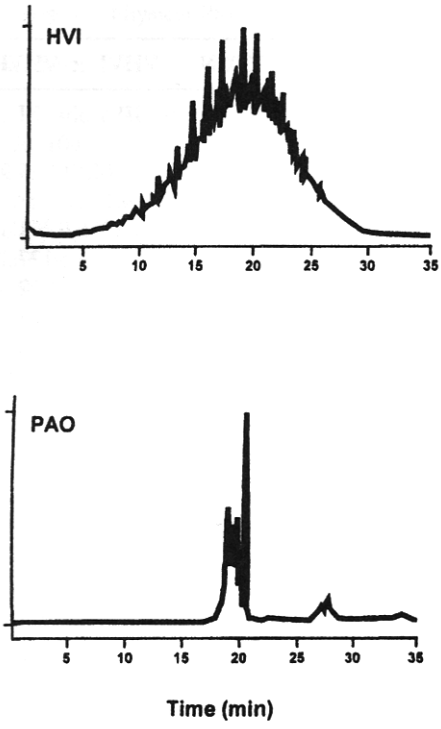

Figure 2 Gas chromatography traces of two 4.0 cSt fluids.

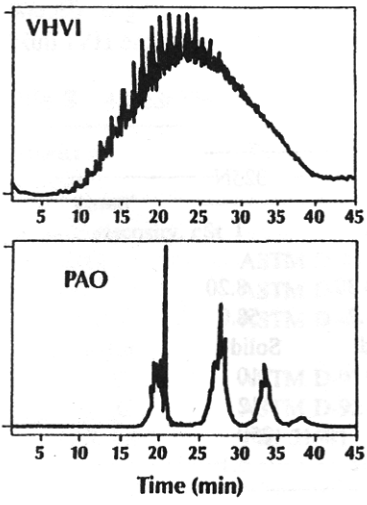

Figure 3 Gas chromatography traces of two 6.0 cSt fluids.

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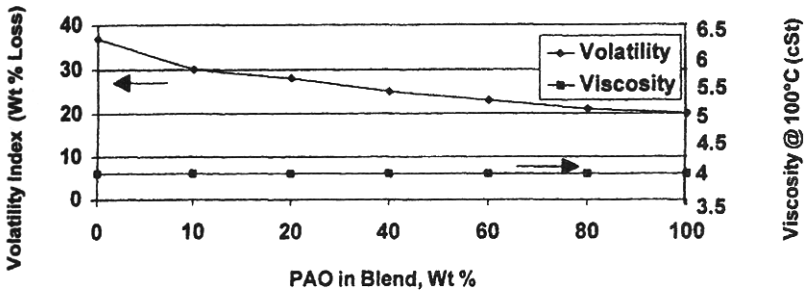

Figure 4 Effect of blending 4.0 cSt PAO with 100N mineral oil. Using an in-house test designed to give approximate correlation to ASTM D-972. (Weight percentage loss after 2.0 hours at 204°C under flow of N_2.)

in the earlier example, contains a wide range of components that degrade performance at both ends of the temperature scale.

3. Properties of Blends

The excellent combination of high and low temperature physical properties of PAOs, combined with their total miscibility with mineral oils, makes them attractive candidates for blending with certain base stocks to improve the base stock quality and bring it into specification for a particular application. This practice has indeed become widespread (but little publicized) as refiners scramble to meet the newer and more stringent API classification requirements.

Figure 4 shows the effect on volatility and viscosity upon blending 4.0 cSt PAO with a light (100N) mineral oil [24]. The "Volatility Index" depicted in this and the following figure is derived from an "in-house" test. A defined quantity of the test sample is placed in a small dish or planchet, which is placed in an oven for 2.0 hours at 204°C. A constant flow of nitrogen is maintained over the sample throughout the test. The values are not the same as obtained in the standard ASTM D-972 or NOACK tests, but they have been shown to correlate well on a relative basis. Small amounts of PAO have a dramatic effect in reducing the volatility of the mineral oil, while having essentially no effect on viscosity. Figure 5 shows the effect of blending the same 4.0 cSt PAO with a heavy (200N) mineral oil. In this case, small amounts of the PAO have a large effect in reducing the viscosity of the mineral oil without increasing the volatility.

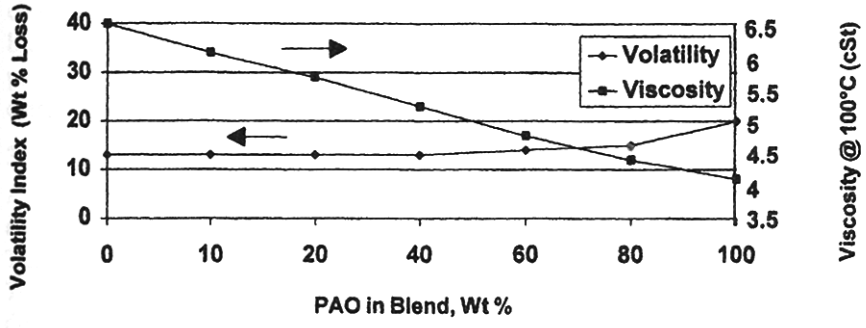

Figure 5 Effect of blending 4.0 cSt fluid with 200N mineral oil. Using an in-house test designed to give approximate correlation to ASTM D-972. (Weight percentage loss after 2 hours at 204°C under flow of N_2.)

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B. Chemical Properties

In addition to the physical properties, the chemical properties of a functional fluid must be considered. The most important chemical property requirements are that the fluid be thermally stable and chemically inert. Under normal operating conditions a working fluid must neither thermally degrade nor react with the atmosphere, the materials of construction, seals, paints, varnishes, performance-enhancing additives, other fluids with which it is intentionally contacted, or inadvertent contaminants.

1. Thermal Stability

Many of the operations calling for a functional fluid are carried out at elevated temperatures. For this reason it is important that the fluid employed not be degraded under the operating conditions. The choice of an appropriate bench test, however, is often difficult. It is important that the test differentiate between thermal and oxidative degradation while simulating real-world operating conditions. It is also important that the test differentiate between thermal degradation and volatility. Some evaluations based on oven aging or thermogravimetric analysis (TGA) have led to erroneous conclusions because the loss in sample weight and/or increase in viscosity could be attributed to volatilization of the lighter components rather than chemical degradation.

One test commonly employed that avoids the danger of misinterpreting volatility for thermal instability is the panel coker thermal stability test. In this test, an aluminum panel heated to 310°C is alternately splashed by the test oil for 6 minutes and baked for 1.5 minutes. At the end of the test, the panels are rated for cleanliness. A completely clean panel has a rating of 10. Table 6 summarizes the results of one study that compared the performance characteristics of mineral oil and various synthetic base stocks for crankcase applications [25]. Under these severe conditions, the mineral oil panel was covered with deposits, indicating a lack of thermal stability. An alkylated aromatic also performed poorly. By comparison, both a PAO of comparable viscosity and a dibasic ester performed well. The best performance was achieved using a mixture of PAO and a polyol ester. Dibasic and polyol esters are commonly used in conjunction with PAO in crankcase formulations.

The thermal stability of PAOs was also investigated regarding use in aviation lubricants [26]. In this evaluation, thermal stability was determined by heating the fluid at 370°C under a nitrogen atmosphere for 6.0 hours in a sealed autoclave. Thermal degradation was measured

Table 6 Thermal Stability Panel Coker Test

Base fluid	Cleanliness
4.0 cSt Mineral oil	0
4.0 cSt PAO	8.0
5.0 cSt Alkylated aromatic	2.0
5.4 cSt Dibasic ester	8.0
4.0 cSt PAO polyol ester	9.5

Test conditions
Panel temperature, 310°C
Sump temperature, 121°C
Operation, 6 min splash/1.5 min bake
Rating system, 10 = clean

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Table 7 Thermal Stability as a Function of Oligmer

	Viscosity loss (cSt)			Oligmer (%)			
	At 250°C	At 300°C	At 371°C	Dimer	Trimer	Tetramer	Pentamer
2 cSt	−0.2	−1.1	−49.9	90	9.0	—	—
4 cSt	−0.9	−5.3	−79.7	0.6	84.4	14.5	0.5
6 cSt	−2.4	−16.9	−88.4	0.1	33.9	43.5	17.4
8 cSt	−4.0	−22.4	−92.3	—	6.0	55.7	27.2
10 cSt	−4.4	−22.9	−94.3	—	1.1	42.5	32.3

by the change in viscosity and by gas chromatographic analysis. The tests show that the thermal stability of PAO products can be ranked as follows:

dimer > trimer > tetramer

These findings are consistent with the molecular structures of the oligomers. The least thermally stable parts of the molecule are the tertiary carbon positions (i.e., the points where there are branches in the carbon chains). The higher oligomers have more branches and are thus more subject to thermal degradation.

Thermal stability as measured by Federal Test Method 79IB (modified) shows that the thermal stability of PAOs is related to the amounts of dimer, trimer, tetramer, and pentamer present (Table 7).

2. Hydrolytic Stability

The inertness of a functional fluid to reaction with water is important for a variety of reasons. Hydrolytic degradation of many substances leads to acidic products which, in turn, promote corrosion. Hydrolysis may also materially change the physical and chemical properties of a base fluid, making it unsuitable for the intended use. Systems in which the working fluid may occasionally contact water or be exposed to high levels of moisture are particularly at risk. Also at risk are systems that operate at low temperature or cycle between high and low temperatures.

The excellent hydrolytic stability of PAO fluids was reported as a result of tests conducted to find a replacement for 2-ethylbutyl silicate ester as an aircraft coolant/dielectric fluid used by the U.S. military in aircraft radar systems [271. The test method required treating the fluids with 0.1% water (or 0.1% seawater) and maintaining the fluid at 170°F (250°F) for up to 200 hours. Samples were withdrawn at 20-hour intervals, and the flash points were measured by the closed-cup method. A decrease in flash point was interpreted as being indicative of hydrolytic breakdown to form lower molecular weight products. The PAO showed no decrease in flash point under any of the test conditions, while the 2-ethylbutyl silicate ester showed marked decreases. Figure 6 shows the results for tests at 250°F.

3. Oxidative Stability.

A high level of oxidative stability is essential to the performance of a functional fluid. In many applications the fluid is required to perform at elevated temperatures and in contact with air. The results from attempts to evaluate fluids for oxidative stability, however, are often confusing. The results are very dependent on the test methodology. Tests involving thin films tend to give different results than tests using bulk fluids. Not only is the presence or absence of metals that catalyze oxidation very important, but different metals interact differently with different fluids. In addition, oxidative stability may be enhanced by the use of antioxidants, but different fluids respond differently to different antioxidants.

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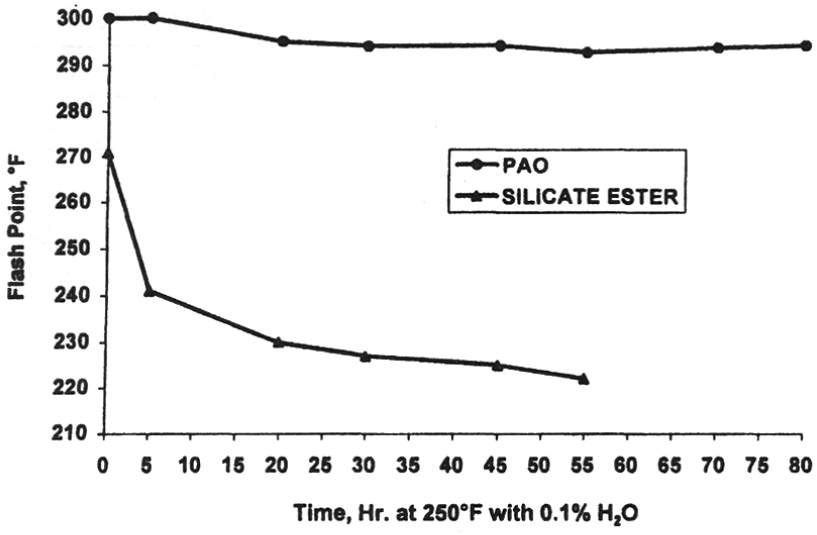

Figure 6 Hydrolytic stability.

One set of experiments that attempted to differentiate between PAOs and mineral oils entailed using differential scanning calorimetry (DSC) [24]. In this test, the fluid is heated in a pan at a controlled rate, and the temperature at which an onset of oxidation occurs is determined by the accompanying exotherm. All the commercial PAO products (with the exception of 2.0 cSt fluid) were tested. The onset temperatures for the six viscosity grades fell in the very narrow range of 187.3–191.6°C. Two 6.0 cSt mineral oils gave values of 189.2 and 200.6°C, respectively. Quite a different result was reported for a laboratory oxidation test in which the fluid was heated at 163°C for 40 hours in the presence of steel, aluminum, copper, and lead coupons [25]. In this test a 4.0 cSt mineral oil exhibited a 560% viscosity increase and a light sludge appearance, while a 4.0 cSt PAO showed only a 211% viscosity increase and no sludge. These results seem to indicate better performance for the PAO, but the loss of weight by the lead coupon in the PAO was 2.8 times that of the coupon in the mineral oil. The same paper reports better performance for mineral oils in a rotary bomb test that measures the time for a specific pressure drop, but better performance for PAOs in beaker oxidation tests where the increase in viscosity is measured.

The failure of unstabilized PAO to outperform unstabilized mineral oil in oxidative stability tests has been tentatively attributed to the presence of natural antioxidants in the latter [28]. The lack of inhibitors in the pure PAO is then given as the rationale for the greater responsiveness of the PAOs to the addition of small amounts of antioxidants. An interesting and somewhat similar rationale has been given for the unusually good responsiveness of PAOs to the addition of antiwear and other performance additives [29]. These researchers from the All-Union Scientific Institute of Oil Refining in Moscow conclude that the efficiency of small concentrations of additives in PAO oils is related to the fast adsorption of the additives on the metal surfaces, because there is little interference of the process in transportation from the bulk oil to the tribo-surface. The low level of interference is a result of weak cohesive forces between the additive molecules and the PAO substrate.

The arguments noted above are supported by results obtained from oxidative stability testing of fully formulated part-synthetic engine oils [30]. A thin-film oxygen uptake test (TFOUT) was used for these studies. This test is a modified rotary bomb oxidation procedure in which

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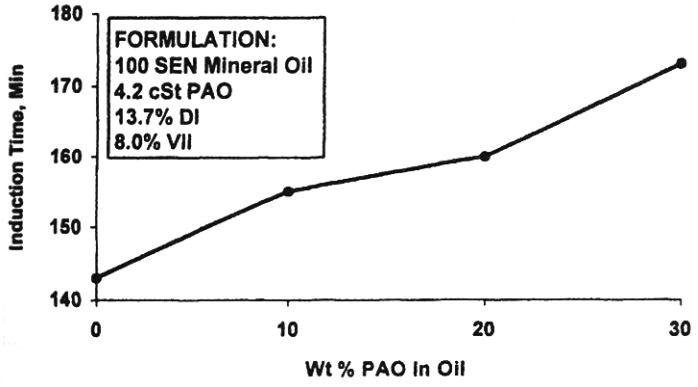

Figure 7 Thin-film oxygen uptake test for fully formulated oils.

the bomb is charged with sample, a small amount of water, a fuel catalyst, and a metal catalyst. The bomb is then pressurized with pure oxygen, placed in a bath at 160°C, and rotated axially at 100 rpm at a 30° angle from the horizontal. The time from the start of the test until a drop in pressure is noted and is defined as the oxidation induction time of the oil. The test oils each contained 13.7% of a detergent-inhibitor package (DI) and 8.0% of a viscosity index improver (VII). The base stock consisted of a 100 SN mineral oil blended with a 4.2 cSt PAO. Figure 7 shows that as the percentage of PAO in the sample was increased from 0% to 30%, the induction time for the onset of oxidation increased from 143 minutes to 173 minutes. Two other papers of interest concerning the oxidative stability of PAOs are also referenced [31,32].

V. APPLICATIONS AND PERFORMANCE CHARACTERISTICS

The use of PAO-based functional fluids is growing rapidly. Conventional applications, such as automotive crankcase, are being spurred on by tighter specifications and an increasing demand for higher performance. Nonconventional applications are also beginning to grow rapidly, especially where specific properties of PAO fluids give them particular advantages in performance, cost-effectiveness, or environmental acceptability. The confidence of original equipment manufacturers (OEMs) in PAO-based synthetic formulations is demonstrated by factory-fill crankcase use in expensive high performance vehicles such as the Chevrolet Corvette and the Dodge Viper.

Porsche has also recently announced the approval of PAO-based full synthetic SAE 5W-40 and SAE 10W-40 Mobil 1 for factory fill for all Porsche passenger cars. Audi uses PAO-based full synthetic (0W-30) in larger automobiles. BMW factory-fill full synthetic gear oils are used for rear axle and manual transmission in passenger cars and Ford-Europe has a factory-fill partial synthetic for its manual transmissions.

A. Overview of Application Areas

Both established and emerging application areas for PAOs are listed below. The list of applications has grown to such a degree in the last few years that a comprehensive review of the PAO performance attributes found advantageous in each and every application would require more space than is available here. Instead, where possible, a reference is cited so that the reader may refer to published information and data in the specific area of interest. Following this section, some performance data for areas of the broadest interest are presented. For detailed reviews of

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the most prominent areas of application, the reader is referred to the appropriate chapters in Part II of this book.

Engine crankcase [33,34]	Compressor oils [38,48–50]
Hydraulic fluids [35]	Heat transfer media [51]
Gear oils [36–39]	Dielectric fluids [24,52]
Greases [4,40–42]	Gels for coating optical fibers [53]
Brake fluids [43]	Off-shore drilling muds [54]
Shock absorbers [44]	Cosmetics and personal care products [55]
Automatic transmission fluids [45]	Textiles [56–58]
Metalworking fluids [46]	Polymers [59]
Pumps [38]	Space applications [60]
Mining and conveyor [47]	Turbine oils [61,62]

B. Performance Testing for Automotive Applications

While physical properties are obviously important in choosing a fluid for a particular application, it is essential that the fluid be subjected to performance testing under conditions that simulate the limits to which the final product will be stressed. But, as indicated above, the list of applications for PAOs is now so long that it precludes a comprehensive discussion of performance testing for all applications. Because the requirements for the wide variety of automotive applications encompass much of the broader spectrum of applications, this section will focus on tests specifically designed and conducted by the automotive industry.

An excellent summary of the automotive testing conducted in the 1970s and early 1980s may be found in a collection of 26 papers published in one volume by the Society of Automotive Engineers (SAE) [63]. In Appendix B of the SAE book, the editors summarize the "eight superior performance features of synthetic engine oils." Their conclusions are based on a compilation of data in the various papers. The eight features they identify are:

1. *Improved engine cleanliness.* This is based on a test using four taxicabs employing a SAE 5W-20 PAO-based oil. Oil changes at 12,000 miles for the first 60,000 miles were followed by a 40,000 "no drain" period.
2. *Improved fuel economy.* The results of 10 different test programs involving a total of 182 vehicles showed a weighted average fuel savings of 4.2%.
3. *Improved oil economy.* In 10 different tests on oil consumption, the percent improvement in miles per quart ranged from 0% (for a military arctic lubricant) to 156%. The average improvement was 55.9%.
4. *Excellent cold starting.* Automobiles with 400 CID V-8 engines could be started at −39°F when the crankcase contained an SAE 5W-20 PAO-based synthetic oil. With a mineral oil of the same viscosity grade the lowest engine starting temperature was −29°F.
5. *Excellent low temperature fluidity.* For the two oils described in item 4, the PAO-based oil exhibited a pour point of −65°F, whereas the mineral oil had a pour point of −37°F.
6. *Outstanding performance in extended oil drain field service.* This conclusion was based on 100,000-mile tests using parkway police cruisers, which are normally operated at speeds ranging from 55 to 100 mph. The test vehicles used a PAO-based SAE 5W-20 "SE-CC" oil. Oil and filter changes were performed every 25,000 miles. The baseline

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consisted of a series of tests carried out in identical vehicles operated on SAE 10W-40 "SE" mineral oil with oil and filter changes every 5000 miles.

7. *High temperature oxidation resistance.* Viscosity increase was measured in a 2-L Renault after 64 hours of operation with an oil sump temperature of 302°F. The synthetic oil showed a 10% increase in viscosity and the mineral oil showed a 135% increase. Both samples were SAE 10W-50 oils.
8. *Outstanding single- and double-length SAE-ASTM-API "SE" performance tests.* The results of all these tests are presented in the reference [63]. The PAO-based synthetic oils met or exceeded all of the requirements.

More recent data show that PAO-based fluids continue to provide superior performance for the increasingly sophisticated cars now being built. Today's automobiles tend to have smaller, more demanding engines. Increased emphasis on aerodynamics means less cooling under the hood, resulting in higher operating temperatures in both the engine and the transmission. In addition to the ability of PAO to meet this challenge with excellent thermal and oxidative stability, PAOs offer another advantage over mineral oils under these severe operating conditions. Both the thermal conductivity and the heat capacity of PAO fluids are about 10% higher than values for the comparable mineral oils. The net result is that PAO-lubricated equipment tends to run cooler. Fully synthetic automotive lubricants for engine oils, automatic transmission fluids, gear oils, and grease applications provide improved protection of hardware [64].

The following subsections examine in somewhat greater detail the results of testing for all the major areas of automotive applications.

1. Crankcase

It is now widely accepted that synthesized fluids, such as poly(α-olefins) and poly(α-olefin)/ester blends, offer inherent performance advantages over conventional petroleum-based fluids for the formulation of modern automotive and commercial engine oils. Proof-of-performance field testing is essential to validate bench test results and document oil quality reserve features [65–70]. The importance of oil quality as a major factor in its durability have been discussed in recent reports [71,72]. Engine oil quality differences can account for differences of two to three times the levels of equipment wear.

Tables 8–11 illustrate the results of tests related to the use of PAO in automotive crankcase applications [24]. Table 8 contains data relating to the hot oil oxidation test (HOOT), which is designed to measure the thermal and oxidative stability of the fluid inside an engine [73]. A PAO and a mineral oil were compared, employing identical additive packages at identical concentrations. In this test air is bubbled through 25 g of the test oil at a rate of 10 L/h for 5 days at 160°C. The oil contains 178 ppm iron(III) acetylacetonate and 17 ppm copper(II) acetylacetonate as oxidation catalysts. The significantly superior performance of the PAO has two possible

Table 8 Hot Oil Oxidation Test (Automotive Crankcase)[a]

	Kinematic viscosity at 40°C (cSt)		
Fluid	Start	Finish	Change (%)
Mineral	95	146.3	54.0
PAO	94	96.8	3.0

[a] Conditions: same additive package at same concentration: temperature, 160°C; time, 5 days. Test described in Ref. 73.

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Table 9 Petter W1 Engine Test[a]

Oil	Grade	Increase (%) in kinematic viscosity at 40°C	Bearing weight loss (mg)
Mineral	15W-40	108	14.1
PAO-25%	10W-40	54	9.7
PAO-50%	10W-40	45	11.5
PAO-100%	15W-40	20	14.5

[a] Conditions: same additive package at same concentration; time, 108 hours.

implications. First, the PAO-based fluid can be used for longer drain intervals, resulting in less downtime and lower maintenance costs. Second, PAO can be used with lower levels of additives and other stabilizers, thus reducing the price differential between PAO and a comparable mineral oil.

Table 9 contains the results of the Petter Wl engine test after 108 hours. The test measures both the increase in viscosity of the fluid and the amount of wear, as determined by bearing weight loss. In this test, the advantages of employing a part-synthetic oil mixture are shown. When PAO is used as only 25% of the base oil, the percent viscosity increase is halved.

The data in Table 10 were acquired from a Sequence III-E engine test, which is commonly used in North America. Table 11 contains data relating to the VW Digiphant test, which is more widely used in Europe. In both tests a 5W-50 full-synthetic PAO-based oil is compared to a 15W-40 mineral oil. As indicated by the SAE classifications, the PAO-based oil is rated for operation at temperatures both lower and higher than the comparable mineral oil based fluid. Nevertheless, the PAO lubricant still outperformed the mineral oil by a wide margin.

The significant performance advantages of PAO-based synthetic engine oils compared to highly refined mineral oils has been reported [74]. Under the high temperature conditions of a quadruple-length (256 h) Sequence III-E test, a PAO-based formulation resulted in excellent performance. Sequence V-E sludge and wear testing is one of the most severe overall passenger car engine oil tests. This test simulates low temperature, stop-and-go driving conditions by measuring sludge, varnish, and wear in a 2.3 L Ford engine. In double-length tests, PAO-based formulations clearly outperformed oils blended with severely hydroprocessed mineral oil.

In triple-length CRC L-38 tests, PAO based formulation showed exceptional wear and corrosion protection.

In diesel engine testing a PAO-based formulation outperformed a commercial oil based on severely hydroprocessed mineral oil. Superior deposit and wear results were found for the PAO-based engine oil. Double-length VW 1431 turbo diesel tests demonstrated the superior thermal-oxidative stability of the PAO-based formulation.

Table 10 Sequence III-E Engine Test (North America)

Oil	Grade	Increase (%) in kinematic viscosity at 40°C
Mineral	15W-40	167
PAO	5W-50	62

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Table 11 VW Digiphant Test (Europe): 147 hours

		Increase (%) in kinematic viscosity	
Oil	Grade	At 40°C	At 100°C
Mineral	15W-40	108	62
PAO	5W-50	25	9

Durability of an optimized PAO-based synthetic formulation compared with a commercial high quality mineral oil was also measured. Chassis rolls testing was done at 55 and at 85 mph with 15,000 mile (24,123 km) oil drains intervals. Wear for the engine having the PAO-based formulation was essentially nil. The engine run on the commercial mineral oil formulation showed several wear parameters that exceeded factory limits. Final proof of performance was evaluated using over-the-road extended drain vehicle tests. In recent extended drain fleet testing studies, PAO-based fully formulated full synthetic oil outperformed mineral oil by having better viscosity control, less oil consumption, and better end-of-test vehicle engine ratings [75].

An added benefit from using synthetic oils over mineral oils (including hydrocracked oils) is the improved performance in regard to filter plugging. Goyal [76] has shown that overall filter life was improved using synthetic oils. The synthetic oils tested showed no filter plugging in extended drain over-the-road tests running up to 25,000 miles (40,000 km).

Synthetic fluids, such as poly(α-olefin)/ester blends, offer a number of inherent performance advantages over conventional petroleum-based oils for the formulation of modern automotive engine oils. Another important feature that must be considered in automotive crankcase applications is low-temperature performance. The most widely recognized property benefit of PAO-based fluids is excellent low temperature performance [77]. Tables 12 and 13 compare the low temperature characteristics of base fluid PAOs with HVI and VHVI mineral oils of comparable viscosity [24]. Highly refined mineral oil stocks are improved over conventional mineral oils; however, they suffer in low temperature performance even with the addition of pour point depressants. The cold crank simulation test is of vital interest to any car owner who has ever lived in a cold climate. The advantage of a PAO-based formulation in the crankcase is immediate and obvious on a cold winter morning—it is the difference between being able to start the car and not. The superior low temperature operation of synthetic automotive lubricants in automotive engine oils, gear oils, and automatic transmission fluid formulations has been demonstrated [78].

Piston cleanliness is another important factor in choosing a crankcase oil. Table 14 presents

Table 12 Low Temperature Performance (Crankcase)

Oil	Kinematic viscosity at 100°C (cSt)	Pour point (°C)	Cold crank simulation, −25°C (mPa · s)	Brookfield viscosity, −25°C (cP)
PAO	3.90	−64	490	600
VHVI	3.79	−27	580	1160
HVI	4.50	−12	1350	Solid
100SN	3.79	−21	1280	Solid

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Table 13 Low Temperature Performance (Crankcase)

Oil	Kinematic viscosity at 100°C (cSt)	Pour point (°C)	Cold crank simulation, −25°C (mPa · s)	Brookfield viscosity, −25°C (cP)
PAO	5.86	−58	1300	1550
VHVI	5.38	−9	1530	Solid
HVI	5.84	−9	3250	Solid
HVI	5.79	−9	2740	Solid
150SN	5.17	−12	4600	Solid

the results of three different tests commonly used to rate piston cleanliness [24]. The PAO formulations performed well compared to the mineral oils, even when used (as in the Fiat test) at only a 15% level in a part-synthetic formulation.

The results of a Caterpillar 1-G evaluation are given in Table 15 [24]. Both a part-synthetic and a full-synthetic PAO-based oil outperformed an equivalent 10W-40 mineral oil.

The high performance of a new synthetic poly(α-olefin)-based SAE 5W-40 heavy-duty oil has been recently demonstrated [79]. This oil exceeds API CG-4, CF-4, CF-2, CF, SH, and EC performance specifications. High performance levels were first measured in standard and extended length laboratory testing. Over-the-road testing using greatly extended oil drain intervals validated high performance levels in Cummins engines. Field testing at extended drain intervals demonstrated performance benefits compared to industry-recognized mineral oil based 15W-40 diesel engine oils.

The successful arctic experience of synthetic based multiviscosity engine oils by me U.S. Army has also been described [80].

2. Transmissions

The advantages of synthetic automotive transmission fluids (ATFs) based on PAO have been recently reported to provide favorable low temperature properties and lower volatility and better wear performance than non PAO-based ATFs [81].

Synthetics have also been promoted as a way to improve bottom-line operating performance by extending component service life and reliability [82].

Hot oil oxidation tests are used to screen oils for use in manual transmissions and rear axles. The test is conducted at 200°C, a more severe temperature than that used in the evaluation of crankcase oils, and the kinematic viscosity at 100°C is measured at specified time intervals. A comparison of the performance of mineral and PAO-based fully formulated oils is shown on

Table 14 Piston Cleanliness

Test	Base oil	Grade	Piston merit
VW1431	Mineral	15W-40	63.70
	PAO	5W-50	72.60
Fiat TIPO	Mineral	15W-40	6.40
	PAO (15%)	15W-40	7.60
MWM	Mineral	15W-40	73.00
"B"	PAO (50%)	10W-40	82.80

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Table 15 Caterpillar 1-G Tests Results for Mineral Oil and Synthetic Formulations

Oil	Grade	Total groove fill (80% maximum)	Total weighted demerits (300 maximum)
Mineral	10W-40	76	294
Part synthetic	10W-40	67	243
Full synthetic	10W-40	53	103

Table 16 [24]. After 16 hours, the viscosity of the PAO fluid had increased only 19%, whereas the viscosity of the mineral oil fluid had increased nearly 500%. After 24 hours, the viscosity of the PAO fluid had increased by only 21%, but that of the mineral oil product had become too viscous to measure.

The HOOT is also used as an indicator of performance for automatic transmission fluids. A less viscous oil is used for automatic transmissions than for manual transmissions (7.5 vs. 10.0 cSt), but the test is still conducted at 200°C. The results of the test are presented graphically on Figure 8 [24]. The PAO-based formulation showed only an 8.6% increase in 100°C viscosity after 24 hours. The viscosity of the mineral oil formulation increased 550% in the same time period.

A 4 cSt fully synthetic ATF has been tested to demonstrate fuel economy potential and the ability to provide adequate transmission performance and protection. The PAO-based ATF demonstrated remarkable lubricant stability. Results showed adequate transmission performance over 20,000 cycles in the GM Dexron II-E cycling test (THCT), light wear of applicable transmission parts, and trace sludge formation [83]. There was no shear-down of the full synthetic. The fluid remained in grade throughout the test.

While the tests described above indicate that PAO-based transmission fluids show better durability and performance than mineral oils at a given temperature, another important phenomenon has been observed. Measurement of transmission lubricant temperatures under high speed driving conditions shows that the synthetic-based oils run as much as 30°C cooler than their mineral oil counterparts [84]. The improved wear characteristics of poly(α-olefin)-based transmission fluid in ASTM D-4172 Shell four-ball testing over mineral oil based formulations has

Table 16 Hot Oil Oxidation Test (200°C): Manual Transmission and Rear Axle Oils[a]

	Kinematic viscosity at 100°C (cSt)	
Time (h)	PAO	Mineral oil
0	10.00	10.50
4	10.45	12.60
8	11.54	12.90
16	11.92	51.24
24	12.10	TVTM[b]

[a] Test described in Ref. 73.
[b] Too viscous to measure.

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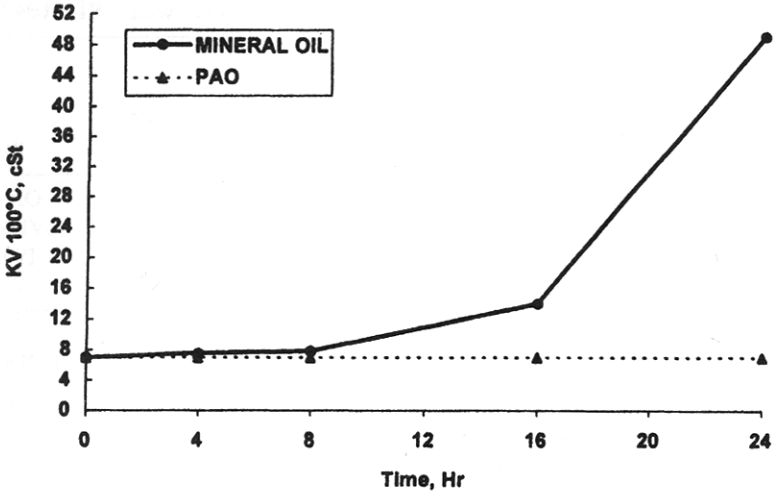

Figure 8 Hot oil oxidation test (automatic transmission, 200°C).

been reported [85]. Lower coefficients of friction were also reported for the PAO-based formulation. Lower temperature and less wear will result in less wear and fatigue failure. A lower rate of oxidation means that replacement of oil will also be reduced. These factors will result in more economical performance—less oil usage and lower maintenance.

3. Gears

The Mercedes Benz spur gear rig performance test is used to evaluate the performance of gear oils. In the test, the elapsed time to gear-tooth breakage is used as the indicator of performance. An SAE 75W-90 synthetic formulation showed a 60% improvement over a SAE 90 mineral oil [24]. The data are presented in Table 17.

4. Seal Compatibility

Seal compatibility is an important factor for any functional fluid. Unlike mineral oils, PAO does not have a tendency to swell elastomeric materials. Early commercial PAO products were not formulated properly to allow for this difference in behavior. Consequently, early PAOs gained an undeserved reputation for leakage. Extensive tests have since shown that the addition of small quantities of an ester to the formulation easily alleviates this problem.

Recent work has indicated that the proper choice of other performance additives may eliminate the need to employ esters, but this approach is not yet in practice for crankcase applications.

Table 17 Mercedes Benz Gear Rig Performance

Oil	Grade	Time to tooth breakage (h)
Mineral	90	85
PAO	75W-90	135

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Table 18 Seal Compatibility (CCMC G5 Specification)

Elastomer	Tensile strength (%)	Elongation (%)	Volume (%)	Hardness (points)
Fluoroelastomer				
150SN	+1.80	−12.0	+1.0	0
PAO	−1.20	−13.0	+0.6	0
Limits	−50/0	−60/0	0/+5	0/+5
Acrylate				
150SN	+5.40	−7.70	+3.40	0
PAO	−12.00	−30.00	−1.50	+4.0
Limits	−15/+10	−35/+10	−5/+5	−5/+5
Silicone				
150SN	−66.0	−60.0	+14.80	−16.0
PAO	−9.60	−15.0	+18.00	−13.0
Limits	−30/+10	−20/+10	0/+30	−25/0
Nitrile				
150SN	+11.0	−11.0	+2.40	+1.00
PAO	+13.0	−19.0	−1.90	+2.00
Limits	−20/0	−50/0	−5/+5	−5/+5

Table 18 shows the results obtained in the CCMC G5 seal compatibility test for base fluids [24]. A 6.0 cSt PAO was compared to a 150SN mineral oil. The four seal materials studied were acrylate, silicone, nitrile, and fluoroelastomer. The seals were evaluated at the end of the test for changes in tensile strength, elongation, volume (seal swell), and hardness. The PAO performance fell within the specification limits for all four elastomers. The mineral oil failed with silicone. Similar tests have been carried out with fully formulated part- and full-synthetic PAO oils. In all cases the fluids met the specifications.

Additional information on choosing the proper seal materials for use with PAO fluids may be found in Refs. 86 and 87.

5. Economy

The performance benefits demonstrated by the various tests that have been described are meaningful to the automotive engineer or tribologist, but the average consumer is most interested in how much savings the use of a PAO-based product is going to generate.

Table 19 describes the results of one study that considered both the increased fuel economy and the extended oil drain interval made possible with part- and full-synthetic PAO crankcase oils. The original calculations [88] have been updated to reflect current prices for gasoline and oil in North America. The calculations are based on 15,000 miles of driving and a "do-it-yourself" oil change regimen. A pump price of $1.20/gal for gasoline has been chosen, and the oil has been priced at $1, $2, and $4/qt for the mineral oil, the part-synthetic, and the full-synthetic, respectively. If the oil is changed every 5000 miles, there is almost no cost differential for the three oils because of the improved fuel economy gained with the synthetics. For the 15,000-mile distance, the saving over the mineral oil formulation is $3 with the part-synthetic oil, and a deficit of $3 is experienced with the full synthetic. If, however, there is only one drain for the full synthetic, the savings goes up to $11. In Europe, where gasoline is much more expensive and the differential in oil prices is less, the savings accrued by the use of synthetic crankcase oils will be much greater.

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Table 19 Automotive Economy

Parameter	Mineral oil	Part synthetic	Full synthetic
Fuel			
Economy, miles/gal	24	24.6 (+2.5%)	25.2 (+5%)
Use, gal/15,000 miles	625	610	595
Cost, $1.20/gal	750	732	714
Savings, $/15,000 miles	—	18	36
Oil			
Cost, $/qt	1	2	4
Cost of three 5 qt changes plus three $5 filters, $	30	45	75
Additional cost, $	—	15	39
Total savings			
Same oil drains, $	—	3	−3
One drain for full synthetic, $	—	3	11

The use of lighter grades of crankcase oil is one answer to the need for increased fuel economy. The possible downside to this strategy would be a concurrent increase in oil consumption and the loss of sufficient high temperature viscosity for adequate engine protection. Studies show, however, that properly formulated PAO-based synthetic crankcase oils, with wide multigrade SAE performance classifications, can outperform mineral oil based formulations in both fuel and oil consumption, while maintaining superior engine protection [63]. Figures 9–12, from this study, illustrate the point.

Figure 9 shows the relative volatility of a 5W-50 full-synthetic formulation compared to five different mineral oil fluids. For European driving, a limit of 13% maximum volatility is specified by ACEA (Association des Constructeurs Européens d'Automobiles) for top grade for passenger car and diesel engine passenger cars and commercial HDDO performance. It may be seen that a 15W-40 mineral oil based formulation is required to meet this specification. The 5W-30 mineral oil formulation, which is used in North America for fuel economy and cold-starting reasons, does not come close to meeting the volatility standard.

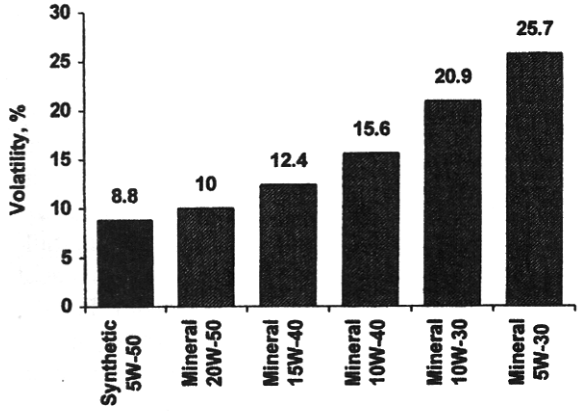

Figure 9 Volatility of fully formulated oils.

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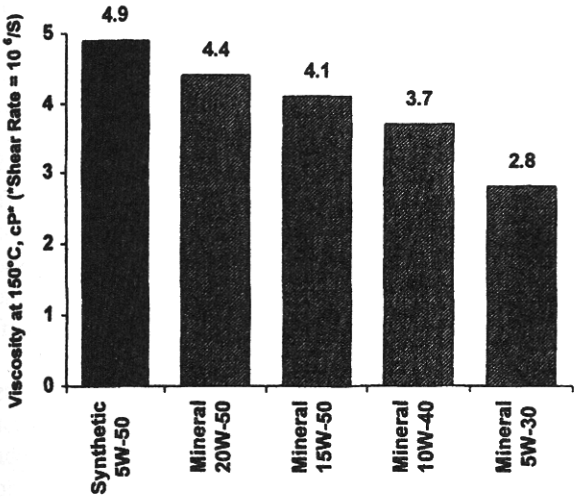

Figure 10 High temperature/high shear viscosity performance of fully formulated oils.

Figure 10 compares the "high temperature/high shear" viscosity at 150°C of the full-synthetic 5W-50 formulation and the mineral oil formulations. The viscosity of the synthetic oil is even higher than the 20W-50 mineral oil. The outstanding performance of the synthetic oil is attributable to the naturally high VI of the PAO in combination with a shear-stable VI improver.

Figures 9 and 10 indicate that oil consumption should be under control with a full-synthetic formulation because of the superior volatility and viscosity performance. Figure 11 shows the results of a 12-car field test, which compared the oil consumption for the 5W-50 synthetic oil and a 15W-50 mineral oil. The oil consumption for the synthetic oil was 25% less than for the mineral oil.

The data presented above for gasoline engines are equally valid for diesel engines. The CCMC D3 standard for superhigh performance diesel (SHPD) engine oils can be met with a

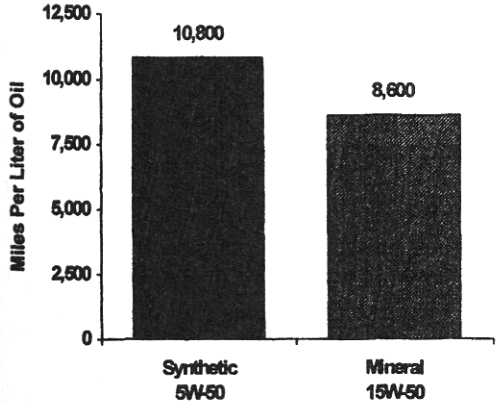

Figure 11 Average oil consumption for a range of modern cars.

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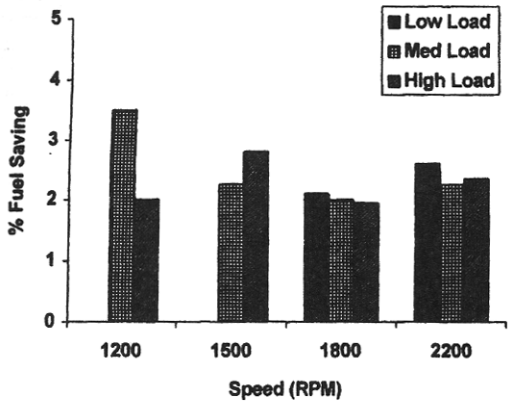

Figure 12 Fuel efficiency: super high performance diesel formulation. Percentage fuel saving for 5W-30 full-synthetic oils is plotted versus saving for 15W-40 mineral oils.

5W-30 synthetic blend. Figure 12 shows that the full-synthetic SHPD oil gave approximately 2% increased fuel efficiency compared to the 15W-40 mineral oil SHPD across a range of typical driving modes.

C. Performance Testing for Industrial Applications

Poly(α-olefins) have served as the lubricant of choice in industrial applications for over a decade [38]. Some of these include sealing fluids and lubricant for pumps handling polystyrene process liquid at 232.2°C (450°F) in nitrogen atmosphere. PAOs have also been used as a replacement for polyolester as a high temperature bearing and gear lubricant in blowers used as steam booster compressors. Rotary and reciprocating mechanical vacuum pumps are lubricated using ISO 46 PAO formulations. The chemical inertness of PAOs has been demonstrated in chemical applications. PAOs give satisfactory performance as:

lubricants for large conveyor chains with exposure to sulfuric acid vapors
lubricants for reactor gearboxes handling nitric and sulfuric acid mixtures
packing seal lubricants for chemical injectors for oil and gas field applications
lubricant/coolant for double mechanical seals of centrifugal pumps handling corrosive, abrasive chloride slurries

Some specific reports of performance advantages in industrial applications are presented next.

1. Refrigeration Compressors

PAOs have also been used in ammonia and fluorocarbon refrigeration compressors because of their low pour points. Other performance advantages reported for PAO fluids include lower operating temperature and less equipment vibration. Bloch and Williams [39] discuss many benefits that high film strength synthetic lubricants offer over other lubricants. Using process plant applications as examples, these authors show that two significant advantages of using high film strength synthetic lubricants are lower operating temperatures (>20°C) and reduced vibration. These two performance advantages increased the life of high torque worm speed reducers by 200–300% and extended oil replacement intervals by a factor of 4 in one application.

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In other applications, in addition to reduced operating temperature and vibration levels, the motor amperages were reduced when the synthetic lubricant was used. Properly formulated high film strength synthetic lubricant based on diesters, PAOs, and combinations of these base stocks can result in reduced bearing and gear operating temperature.

2. Gear Oils

The use of PAO-based gear oils in industrial settings can lead to important savings in energy consumption, as well decreased downtime and lower maintenance requirements. The wide range of operating temperatures allows the use of less viscous oils, which results in greater energy efficiency. The relatively low coefficient of friction for PAOs reduces the amount of internal friction created by the normal shearing of an oil film during operation.

Improved scuffing performance for gear/circulating oils has been demonstrated by Jackson et al. [89], who studied the influence of lubricant traction characteristics on the load at which scuffing occurs. The study compared low traction PAO-based lubricants with mineral oils in additive-free, antiwear, and extreme pressure (EP) formulations. Benefits of 25–220% were observed for the PAO-based synthetic lubricants over mineral oils. The investigators found that low traction PAO-based lubricants uniformly gave higher scuffing loads per unit width than the mineral-based fluids tested at both high and low specific film thickness. PAO-based gear and circulating oils outperformed mineral oil based gear and circulating oils, respectively. PAOs were also shown to be very responsive to additives.

The advantages of PAOs as lubricants in conveyor applications has been demonstrated by Paton et al. [47]. Gearboxes lubricated with a fully synthetic poly(α-olefin)-based gear oil (75W-90) was studied. An all-season PAO-based fluid was chosen for pulley shaft bearing lubrication.

In wind turbine gearboxes, the high viscosity index of a synthetic fluid would ensure that the change in viscosity with temperature would be less than with equiviscous mineral oils. A further advantage of a synthetic fluid for applications of these types is that synthetics have lower pour points than mineral oils [61]. PAOs provide both excellent viscosity index and low pour point. These properties make them a fluid of choice for applications characterized by wide ranges of operating temperatures.

Table 20 is a compilation of data from 10 reports relating to the benefits of increased efficiency found when industrial transmissions were switched from a mineral oil to PAO-based gear oils [90–99]. The increases ranged from 2.2 to 8.8%. It is interesting to note that the efficiency increase observed in worm gears has a close positive correlation with the reduction

Table 20 Industrial Gear Oil Applications

Transmission type	Reduction ratio	Power (hp)	Load (% rated)	Efficiency increase (%)
Worm gear	10:1	3.0	100	2.2
Worm gear	15:1	1.55–2.0	100–130	3.8
Worm gear	25:1	6.5–8.1	100	4.4
Worm gear	30:1	3.2–3.9	96–117	5.6
Worm gear	50:1	3.0–6.0	100–200	7.7
Worm gear	50:1	0.5–1.0	50–100	8.8
Spur gear/chain	—	35	—	2
Spur gear	24:1	200	—	6
Series of nine worm gears	15:1	122–142	100–112	6
Series of five worm gears	39:1	75	—	5.8

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ratio. This correlation exists even though the data were reported by different companies and collected on different types of equipment.

3. Turbines

Wind turbine gearboxes are also subject to wear and pitting fatigue failure. Water contamination can also occur. Among the many lubricant-related factors, film thickness under operating conditions must be considered in the formulation of a wind turbine lubricant. Excellent low temperature properties and high load performance are possible with a PAO-based wind turbine lubricant (Tribol 1510) [62].

PAOs have been employed in larger General Electric and EGT industrial gas turbines. Oils used in these applications must have enhanced oxidation resistance to withstand journal heat soak temperatures that can go as high as 250–300°C. Mineral oils volatilize and form deposits, whereas lubricants formulated with PAOs give cleaner running performance and extended useful life of the lubricant (from 4–5 years up to 15 years) [62]. Mobil Industrial Lubricants has developed Mobil SHC 800 for land-based gas turbines. This fluid, based on PAO, provides low maintenance and reliability over wide temperature ranges.

4. Hydraulic Oil Performance

PAOs offer a variety of property/performance features and benefits that cannot be achieved using alternative base fluids. PAOs have excellent low temperature fluidity and excellent viscosity index when compared to all but the most expensive base fluids. PAOs have very low volatility and excellent hydrolytic, thermal, and oxidative stability relative to many other oils.

5. Metalworking Performance

Antiseizure properties of lubricants, as measured by their maximum workable die temperature (MWT), have been reported [46]. The maximum workable die temperature of lubricating oils reported were as follows: PAO oils, 160–170°C; polybutene oil, 150°C; mineral oils, 100–120°C; ester oils, 90°C. Addition to mineral oils or PAOs of phosphorus-containing extreme pressure agents enhanced the workable die temperature to about 300°C.

6. Cost Savings

The open literature contains a number of reports of savings obtained by industrial concerns that switched from a mineral oil to a PAO-based gear or bearing oil. Table 21, a short tabulation of some of these reports [100], shows diverse types of manufacturing and a diverse selection of applications for which the PAO-based lubricants were applied. The annual savings for these companies ranged from $12,000 to $98,000. The largest reported savings in Table 21 ($98,000/year) was achieved when a PAO-based gear oil was used on the felt roll bearings in a paper

Table 21 Savings with PAO-Based Gear Oils

Company type	Application	Annual savings
Soybean processing	Aeration blower	$2100/unit
Plastics	Bearing circulation system	$12,000
Copper wire	Line gears	$19,000
Paper mill	Felt roll bearings	$98,000
Steel mill	Fly ash blower shaft thrust bearings	$77,000
Pharmaceutical	Gear reducers	$70,000
Aluminum cans	Gear reducers	$35,000
Manufacturing	Various	$80,000

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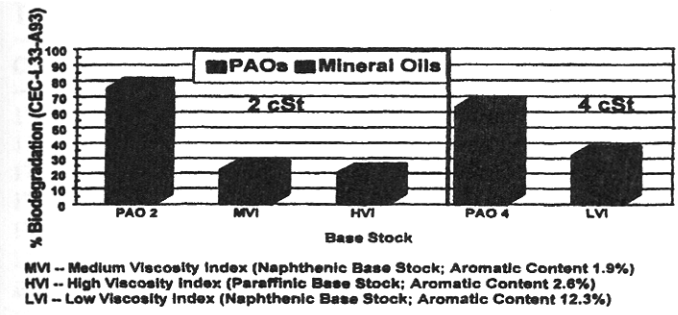
% Biodegradation (CEC-L-33-A93)
PAOs Mineral Oils
2 cSt
4 cSt
PAO 2
MVI
HVI
PAO 4
LVI
Base Stock
MVI -- Medium Viscosity Index (Naphthenic Base Stock; Aromatic Content 1.9%)
HVI -- High Viscosity Index (Paraffinic Base Stock; Aromatic Content 2.6%)
LVI -- Low Viscosity Index (Naphthenic Base Stock; Aromatic Content 12.3%)

Figure 13 Biodegradability of base stocks poly(α-olefins) versus equiviscous mineral oils: MVI, medium viscosity index (naphthenic base stock, aromatic content 1.9%); HVI, high viscosity index (paraffinic base stock, aromatic content 2.6%); LVI, low viscosity index (naphthenic base stock, aromatic content 12.3%).

mill. The high speed of the huge rolls in a paper mill is critical to their competitive operation, and the use of PAO-based fluids is becoming an important part of the overall strategy for cost-effective operation.

D. Applications Sensitive to Health and Environmental Issues

Published results demonstrating the favorable biodegradability of PAO fluids are available [101–103]. In a comparison of PAOs with equiviscous mineral oils, PAOs were found to be significantly more biodegradable (Fig. 13).

Time-extended CEC L-33-A-94 testing has also shown that 2, 4, and 8 cSt PAOs continue to biodegrade well past the 21-day period prescribed in the standard method (Fig. 14).

PAO fluids are also considered to be nontoxic and nonirritating to mammals (Table 22).

PAOs are not expected to be toxic to aquatic organisms. For example, in the Microtox test with bioluminescent bacteria, there were no effects for 49,500 ppm of the water-soluble fraction (Table 23).

Results have also been presented that demonstrate that low viscosity (2 and 4 cSt) PAOs are significantly biodegradable (in the CEC L-33-T82 biodegradability test) [104].

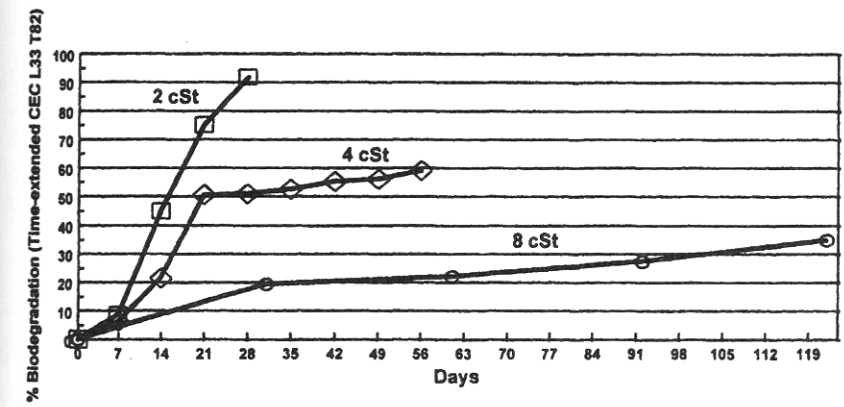

Figure 14 Biodegradability versus time for PAO fluids.

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Table 22 Acute Mammalian Toxicity of PAO Fluids

PAO Fluid	Oral LD_{50}[a]	Skin irritation[b]	Eye irritation[c]	Comedogenicity[d]
2 cSt	>5 g/kg	Negative	Negative	Negative
4 cSt	>5 g/kg	Negative	Negative	Negative
6 cSt	>5 g/kg	Negative	Negative	Negative
8 cSt	>5 g/kg	Negative	Negative	Negative
10 cSt	>5 g/kg	Negative	Negative	Negative

[a] Rat oral LD_{50} (statistically calculated dose needed to kill 50% of the rats in the study) is determined by single-dose administration of undiluted test material. Rat oral LD_{50} values of >5 g/kg are considered nontoxic.
[b] Where heated material or oil mists could be generated, consult the MSDS for recommended handling procedures.
[c] According to criteria of the federal Hazardous Substance Act (FHSA, 16 CFR 1500).
[d] The ability of the test material to induce the enhanced collection of increased sebaceous material and keratin likened to acne blemishes.

1. Food Contact

PAO base stocks are pure, saturated hydrocarbons. They contain no aromatics (except for small amounts in the 40 and 100 cSt fluids produced by Mobil) and no functional groups. As such, the toxicity is expected to be as low or lower than the most highly refined white mineral oils.

The PAOs have Food and Drug Administration (FDA) approval for use in both "indirect" and "incidental" food contact applications. They fall within the definition of a white mineral oil according to the Code of Federal Regulations (21 CFR 178.3620, paragraph B). The applications for which FDA approval is required, and for which PAO is qualified, are listed in Table 24.

In essence, PAO fluids may be used as a component of any material that contacts food or as a lubricant for any machinery that processes food. Direct food contact approval (i.e., as a component to be purposely ingested) has not yet been obtained in the United States, but probably could be obtained if an application developed that warranted the effort and expense of obtaining the approval. Neste's food grade PAO fulfills 21 CFR 172.878 and 178.3620a for direct food

Table 23 Acute Aquatic Toxicity of the Water-Soluble Fraction of PAO Fluids by the Microtox® Method

PAO fluid	EC_{50} (5 min)[a]
2 cSt	NR
4 cSt	NR
6 cSt	NR
8 cSt	NR
10 cSt	NR
40 cSt	NR
100 cSt	NR

[a] EC_{50}, median dose resulting in contamination; NR, no observable effects at concentrations up to 49,500 ppm.

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Table 24 FDA-Approved Applications for PAO

CFR section[a]	Application
175.105	Adhesives
176.200	Defoaming agents used in coatings
176.210	Defoaming agents used in the manufacture of paper and paperboard
177.2260	Production of resin-bonded filters
177.2600	Rubber articles (plasticizers) intended for repeated use
177.2800	Production of textiles and textile fibers
178.3570	Lubricants with incidental food contact
178.3620b	Technical grade white mineral oil
178.3910	Surface lubricants used in the manufacture of metallic articles (e.g., metallic foil)

[a] Food and Drug Administration, HHS-21 CFR Ch. 1, April 1, 1988 ed.

contact. Neste has approval for PAO 6 (food grade) as a food additive in Finland. Work is proceeding to get Europe-wide approval for PAO (food grade) as a food additive. Neste has been selling PAO 6 (food grade) for use as a glazing agent for sweets in Finland since 1992.

PAO specifications for food additive use in Finland are very strict on purity. There can be no oxygen-containing components, and hydrogenation of the poly-1-decene must be complete. One test that is used to check purity is the "hot acid test," also referred to as the "readily carbonizable substances test," described in the pharmacopoeias.

2. Cosmetics and Toiletries

PAO fluids are nontoxic when given orally to rats. The lethal dosage for 50% of the test subjects (LD_{50}) is greater than 5 g/kg of body weight. PAOs are also nonirritating to the eyes and skin of test animals, and they are not expected to induce sensitization reactions. They have low vapor pressures and therefore are not hazardous if inhaled. Subjectively, PAOs are said to have a better "feel" on human skin than white mineral oils. For all these reasons, a small but growing market for PAO is developing in the cosmetics industry [55]. A national brand of lipstick contains PAO as a major component and in Europe PAOs (polydecene) can be found in a variety of cosmetic products such as makeup removers, body oils, shower and bath oils, and makeup cremes.

3. Offshore Drilling

Regulations on the marine toxicity of fluids used to lubricate the drill head in offshore drilling operations are becoming tighter, especially in the North Sea. PAO fluids have been used as a base stock for synthetic-based drilling fluids in offshore applications. The purpose of these fluids is well bore cleaning, bit cooling and lubrication, and shale stabilization. The discharge of cuttings using synthetic-based muds is considered less harmful to the marine environment. PAOs offer excellent marine toxicity values. This technology, developed in the early 1990s [105,106], has been displaced by alternative technologies. Leading alternative technologies include linear α-olefins [107] and isomerized olefins [108].

4. Miscellaneous

Other environmentally sensitive areas for which PAO fluids are being evaluated are logging operations (chain saws), marine outboard engines, and hydraulic systems for large farm machinery. In addition to low toxicity, it is important that fluids used in these applications exhibit biodegradation and low levels of bioaccumulation. Preliminary evaluations indicate that PAOs do not bioaccumulate and that their rate of biodegradation is faster than that of mineral oils of

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Table 25 Military Applications

Specification number	Applications	Lubricant highlights
MIL-H-46170	Type I: tank recoil and hydraulic systems	4 cSt PAO: ester: (TCP)
	Type II: aerospace test stands	PAO base stock specs Finished fluid specs
MIL-H-83282	Aircraft and missile hydraulic systems	4 cSt PAO: ester: TCP PAO base stock specs Finished fluid specs
MIL-H-83282 (low temperature)	Aircraft and missile hydraulic systems	Dimer/trimer ~3 cSt PAO: ester: TCP *No* pour point or VII additives Finished fluid specs only
MIL-G-10924	Multipurpose grease for all ground vehicles, artillery, and equipment	Typically 6 cSt PAO base stock Finished grease specs only Formulation and constituents Confidential and proprietary
MIL-L-63460	Small- and large-caliber weapons cleaner, lubricant, and perservative, −65 to 150°F	Mineral oil and/or synthetic based 2 and/or 3 cSt PAO Finished lube specs only
MIL-L-2104	Internal combustion engine oil and power transmission fluids All types of military tactical/combat ground equipment	Mineral oil, synthetic, or combination base stock
MIL-L-2105	Gear oil for units, heavy-duty industrial-type gear units, steering gear units, and universal joints	Mineral oil, synthetic, or combination base stock Finished lube specs by grade only
MIL-C-87252	Dielectric coolant for electronic applications Hydrolytically stable Replacing silicate ester coolant	PAO base stock specified 2 cSt Dimer ~99.5% PAO Oxidation/corrosion inhibitor Finished fluid specs only

comparable viscosity. On the other hand, the rate of biodegradation is slower than for some ester-based drilling muds also being evaluated for this application. For a full discussion of this very complex issue, the reader is referred to the chapter by Droy and Randies.

E. Military Applications

The earliest applications for PAO fluids were in the military. MIL-H-83282 is a specification for a hydraulic fluid for jet aircraft. The specification was built around an experimental 4.0 cSt decene-based PAO produced by Mobil in the late 1960s. The requirements included extreme low temperature fluidity as well as high flash and fire point values. The latter requirement was to minimize the risk of loss due to fire in the event that a hydraulic line was severed by gunfire. MIL-H-83282 remains an important military fluid today.

An interesting, if not publicized, example of superior performance for PAO came to light as a result of the war in the Persian Gulf in January 1991. Under harsh desert conditions, the U.S. weapons that were lubricated and cleaned with PAO-based oils performed better than similar Allied weapons using conventional fluids, resulting in some rush orders to the lubricant formulators from Allied commanders.

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Table 25 contains a short summary of military specifications that either require or often use PAO fluids.

F. Space Applications

Precision spacecraft mechanisms require critical selection of lubricants to maximize reliable performance in space, where low or no maintenance is the rule. Communication, global surveillance, meteorological, and navigational spacecraft contain a variety of moving mechanical assemblies (MMAs). These mechanical subsystems have become life-limiting for many spacecraft [60]. Most problems have been lubricant-related problems including loss of bearing contact and/or chemical degradation. Results of recent studies advocate the use of formulated poly(α-olefin) oils and greases for most high cycle precision bearings [60].

VI. MARKETS AND PRODUCTION CAPACITIES

By the end of 1990, world PAO demand had grown to 188.4 million (MM lb) [9]. This volume, a remarkable 14-fold increase since 1975, still represented less than 0.05% of the total world lubricant base stock market at that time. By the end of 1993, world PAO demand had grown to 260 MM lb [109]. U.S. capacity as of June 1, 1993, was reported at 287 MM lb [110] and is predicted to grow to 458 MM lb/yr by the year 2000 [109].

During 1975–1980, demand for PAO grew at 33% per year. Synthetic engine oils were a novelty on the market during this period, and they were growing from a base near zero. Growth slowed during the 1980–1985 period to around 7%. Some early product entrants to the market were improperly formulated, and the resultant poor performance attached some stigma to the use of synthetics. The 1985–1990 half-decade saw a strong new interest in synthetic lubricants because of the enactment of stringent specifications and governmental regulations that were difficult to meet with mineral oil base stocks. The growth rate for PAO during this period was approximately 19% per year.

A. Demand by Segment and Region

Strong growth for the PAO market is predicted to continue in the foreseeable future. Table 26 shows the expected rate of growth for PAO into the automotive, industrial, military, and emerging market segments. The total market was expected to grow from 185 MM lb in 1990 to 450 MM lb in 1995—an annual growth rate of about 20% per year [24,100].

Although the PAO markets in 1990 were approximately the same size in Europe and North America, the breakdown by segments was considerably different. The European market was driven primarily by the automotive demand, whereas the North American market was more balanced. In Europe, 78% of the PAO demand was for the automotive sector, with the rest going

Table 26 PAO Market Segment

Segment	1990 (MM lb)	Predicted 1995 (MM lb)	Predicted growth rate (%/year)
Automotive	110	230	18
Industrial	55	100	13
Military	15	20	6
Emerging	5	100	85
Total	185	450	

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Table 27 PAO Market Segment Growth by Region

Region and segment	1990 (MM lb)	Predicted 1995 (MM lb)	Growth rate (%/year)
North America			
Automotive	35	100	23
Industrial	35	60	11
Military	15	20	6
Emerging	5	40	51
Total	90	220	
Europe			
Automotive	70	110	10
Industrial	20	40	15
Military	—	—	—
Emerging	—	60	N/A
Total	90	210	
Far East			
Automotive	4	15	30
Industrial	1	5	38
Military	—	—	—
Emerging	—	—	—
Total	5	20	

into industrial applications. In North America, the automotive and industrial markets each took about 38% of the PAO, while the military used 17%. The remainder went into "emerging" markets, which are discussed in more detail later.

Table 27 is a breakdown of PAO market growth by both segment and region. It should be noted that the 1995 forecasts predicted the convergence for demand distributions by segment for PAO in Europe and North America. North America in fact began catching up with Europe in the automotive applications area while Europe began catching up with North America in industrial applications. Both continents undertook vigorous development of the "emerging" segments. Accurate numbers for market segment for 1995 were not available to the authors at the time of publication, however, overall market growth and trends are consistent with the predictions made earlier.

The development of markets and applications for PAO have been generally confined to North America and Europe. In 1990 the Far East accounted for only 2.7% of the demand for PAO. Between 1990 and 1995, the consumption of PAO in the Far East grew at an annual rate of about 30%—reminiscent of the growth in the West during the 1975–1980 time frame.

B. Emerging Markets

A substantial portion of the growth being forecast for PAO has been described as "emerging" markets. The term "emerging" is used to designate application areas in which there is a high potential for PAO to capture a part of the market now being serviced by other types of fluids.

Table 28 lists seven areas in which PAO fluids and formulations are continuing to be developed to fulfill specific requirements not being met by the fluids currently in use. The three driving forces for shifting from the current functional fluid to PAO are cost, performance, and toxicity.

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Table 28 Emerging Markets

Product line	Current volume (MM lb)	Fluid type[a]	Driving force
Polymer	200	WMO[a]	Toxicity/performance
Personal care	150	WMO/esters[a]	Toxicity
Refrigeration	45	Polyalkyl glycols	Performance
Textile	25	Silicones/WMO	Cost and performance
Dielectric fluids	90	Mineral/silicones/PCB	Cost/performance/toxicity
Brake fluid	440	Polyethylene glycol/silicones	Cost and performance
Shock absorbers	110	Mineral oil	Performance
Total	1060		

[a] WMO, white mineral oil; PCB, polychlorinated biphenyl.

C. PAO Production Capacity

At the end of 1990, the worldwide production capacity for PAO was 325 MM lb/yr. Sales for 1990 were 57% of production capacity, which represented a major reversal of the demand/supply situation of the mid-1980s. Because of the shortage of PAO available earlier, formulators were forced to seek alternative (if sometimes less satisfactory) solutions for their performance requirements. There was a strong and understandable hesitancy among equipment manufacturers, formulators, and end users to place themselves in a precarious supply situation. As a result of the excellent supply situation that now exists, there is a new surge of activity in the development of new markets and applications for PAO fluids.

Table 29 is a summary of the PAO producers and their capacities in 1990. Ethyl Corporation brought their 80 MM lb/yr plant in Feluy, Belgium, onstream in January 1991. As mentioned earlier, in 1994 Ethyl split off Albemarle as a separate company, which owned and operated the PAO business until March 1996, when Amoco purchased the α-olefin and PAO business from Albemarle. In 1991 Neste brought their 45 MM lb/yr plant in Berigen, Belgium, onstream. PAO production capacities as of 1993 are summarized in Table 29. A summary of synthetic

Table 29 Worldwide PAO Capacity (MM lb/yr): Low and High Viscosity

Manufacturer	1990	1993 [109]	Predicted 1996 [112]
Amoco	0	0	249
Albemarle	0	256	0
Ethyl	170	0	0
Mobil	80	157	224
Chevron	55	88	53[a]
Exxon	20	0	0
Neste	0	66	62
Uniroyal	0	0	4.4
Total	325	567	592.4

[a] This value appears low based on the 1993 reported value. No indication has been made that capacity has been reduced since Chevron's expansion prior to 1993.

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lubricants including markets and consumption for PAOs has been published [111], and price–performance data are available as well [112].

D. Competitive Products

Highly refined mineral oils approach PAO in some performance characteristics. These mineral oils fall into three categories, as explained in the subsections that follow.

1. Very High Viscosity Index (VHVI) Oils

The premier product derived from crude oil sources is Shell Oil's patented extra high viscosity index (XHVI) oil. It is produced in France and Australia from a special cut of refinery slack wax by a severe hydrocracking procedure. Shell's capacity is 150 MM lb/yr. Shell is apparently currently manufacturing XHVI base stocks from syngas in Malaysia. The product exhibits very good performance characteristics, but it is deficient relative to PAO in both low temperature properties and volatility (Table 4).

Petro Canada has recently begun production of a 100 MM gal/yr base oil plant in Ontario [113]. This production includes a series of severely hydroprocessed mineral oils (VHVI fluids) under the name of Phoenix. These generally have higher pour points and higher NOACK volatility than the equiviscous PAOs, but are improved over conventional mineral oil base stocks.

BP currently manufactures LaVera Hydrocracked Residue (LHC) fluids in LaVera, France. LHC fluids are available in 3, 4, 6, and 8 cSt grades. Processing consists of hydrocracking of a middle distillate stream, followed by vacuum distillation and a dewaxing step. These stocks are wax isomerates that are highly isoparaffinic.

Chevron has also recently announced that it will produce unconventional base oils (UCBOs) at its lubricant base oil facility in Richmond, California. These new base oils are reported to be in the range of 115–135 VI [114].

Conoco and Pennzoil have announced a joint venture, Excel Paralubes, to produce 18,000 barrels of base oil per day at Conoco's plant in Lake Charles, Louisiana. These materials are subjected to Chevron's isodewaxing process to produce higher quality base stocks [113]. Under the name Hydroclear™, Conoco is marketing a new line of clear lube oils produced using hydrocracking technology.

The base oil plant of Yukong Ltd. in South Korea produces VHVI base stocks using a combination of hydrocracking and catalytic dewaxing processes developed by Yukong with Raytheon Corporation.

2. High Viscosity Index (HVI) Oils

HVI base stocks are intermediate in properties between the VHVI fluids and conventional solvent-refined oils (Table 3). HVI oils are manufactured by a process that involves hydrotreating, redistilling, and solvent refining. HVI fluids were first produced by British Petroleum in 1976 and are now produced by BP at LaVera and Dunkerque in France. HVIs are also produced by Modrica in Yugoslavia and DEA in Germany. HVI fluids are less costly than either PAO or VHVI fluids, but 1.4–2.0 times more material is generally required to blend with an off-spec mineral oil to bring a formulation into 10W-30 specifications.

Exxon has begun providing screening samples of its new RHC™ (raffinate hydroconversion) base stocks, which it plans to produce at its Baytown, Texas refinery in 1999. These high viscosity index oils will be in the range of 105–120 VI.

3. Poly(internal)olefins (PIO)

PIO fluids are similar to PAO fluids in that both are manufactured by the oligomerization of linear olefins. The olefins used for PIO manufacture, however, are derived from the cracking

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of paraffinic base stocks. The internal olefins are more difficult to oligomerize than the α-olefins derived from ethylene chain growth, and the products have VIs that are 10–20 units lower than those of comparable PAOs.

VII. CONCLUSION

A number of forces will drive the growth of high performance functional fluids for the next decade and beyond. These forces derive from diverse societal needs, but they have a common goal rooted in the uniquely human belief that there must be a better way to do whatever it is that has to be done. Some of these forces and the consequences they imply for the growth of PAO fluids include the following.

A. Regulatory

U.S. regulations for corporate average fuel economy (CAFE) are having a significant effect in both the design of new automobiles and the lubricant requirements and recommendations for them. To meet the fuel economy standards, which will now include a cold-start cycle specification, the OEMs are being forced into recommending SAE 5W multigrade crankcase oils. In addition, increased emphasis on aerodynamics results in higher engine operating temperatures, which affects not only the crankcase lubricant but also the transmission fluid, the gear oils, and the greases. All these factors will require fluids with lower low-temperature viscosity coupled with lower volatility, higher thermal and oxidative stability, higher heat capacity, and higher heat conductivity.

Regulations in the areas of consumer protection, worker safety, and the environment are becoming increasingly stringent in their requirements for nontoxic, nonhazardous, environmentally friendly products. Regulatory agencies are beginning to recognize potential toxicological problems associated with white mineral oils. PAOs are being put forward as high performance, safe substitutes.

B. Performance and Cost-Effectiveness

The need for improved performance remains a critical factor in the drive toward increased usage of PAO-based lubricants and functional fluids. In many applications mineral oil based products either cannot meet the more stringent requirements or are only marginally satisfactory. The use of PAO for blending with marginal base stocks to bring them into specification is increasing.

Fleet operators, who are much more sensitive to cost-effectiveness than the general public, will continue to increase their usage of synthetics as they recognize the potential long-term savings.

Operators of large industrial machinery are beginning to recognize the increased cost-effectiveness of lubrication with PAO-based products. Machines operate at lower temperatures, are less subject to wear, require less maintenance and downtime, consume less oil, and operate longer between lubricant drain cycles. The value of PAO-based products for the lubrication of heavy-duty, off-road mobile equipment is also being recognized, especially where routine maintenance is difficult.

C. Original Equipment Manufacturers (OEMs)

The diversity and uneven regional availability of mineral oil base stocks hinder standardization based on mineral oils. In applications for which performance requirements are exacting, there will be a shift by OEMs to assure uniformity by requiring synthetic fluids.

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Industrial and automotive OEMs are pushed by the consumer and by the competition to extend warranty periods. At the same time, OEMs are under pressure to reduce the required amount of maintenance and downtime. Both avenues may be addressed by switching from mineral oil to PAO-based fluids. General Motors used a full-synthetic, PAO-based oil as the factory-fill and recommended crankcase fluid for the first time when it introduced the 1992 Chevrolet Corvette. Today, fully synthetic PAO-based oil is still recommended for the high performance vehicle.

The latest trend to address consumer convenience as well as protection of equipment from inadvertent contamination of the working fluid is the "fill-for-life" concept. General Motors is studying a "fill-for-life" PAO-based automatic transmission fluid for its future models.

D. Petroleum Companies and Blenders

Lubricant producers have historically had low profit margins. Base stock prices have been closely tied to crude oil prices, and the selling price for finished fluids has remained tied to base stock costs. Lubricant companies are beginning to recognize that high performance, high image products based on PAO afford the opportunity for higher selling prices and increased margins. European companies have been the leader in this regard, but North American companies are expected to catch up. While Mobil Oil has been the leader in the United States with Mobil 1 since the mid-1970s, most of the major lubricant producers have introduced, or plan to introduce, full-synthetic motor oils to the market in 1990s.

Another large factor in the forecasted growth for PAO is the recognition that there are insufficient high quality base fluids to meet new product requirements. PAOs will be used to blend mineral oil stocks into specification. Some of these products will be sold and marketed as "part-synthetic" oils at a price between the top tier mineral oils and the "full synthetics." In other cases, the blender or formulator will use PAO in an "in again–out again" basis, depending on the availability of mineral oil base stocks of sufficiently high quality. In these cases, consumers will never know they have purchased a "part-synthetic."

E. Consumer

The role of the consumer will be important to the growth of PAO fluids. Manufacturers' recommendations will have little effect if the consumer does not pay attention to them. Studies show that the traditional attitude in the United States (i.e., that all oils are "pretty much the same") is beginning to change. Consumers are becoming more aware of issues such as fuel economy, cleaner air, higher performance, lower maintenance, and longer vehicle life. All these concerns, coupled with the increased availability of oils to meet the demand, will lead to a shift by a segment of the consumer population toward the premium synthetic oils.

F. New Technology

The final area poised to provide an impetus to the increased use of PAO fluids is the development of new technology. Two areas are clearly important. The first is the development of new additives and formulation packages specifically for use with PAO fluids. Formulation development is being actively pursued by PAO producers, additive manufacturers, formulators, lubrication specialty companies, and OEMs. Some of this work is in the form of joint efforts, and much of the information being developed is proprietary.

The second important area to be impacted by new technology is the development of new PAO fluids from new starting materials and/or with new catalyst systems. The objective in this research is to produce products with particular characteristics needed for specialty applications.

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Table 30 Physical Properties: Effect of Olefin Chain Length

Property	Test method	Carbon number of initial olefin			
		8	10	12	14
Kinematic viscosity, cSt					
At 100°C	ASTM D-445	2.77	4.10	5.70	7.59
At 40°C	ASTM D-445	11.2	18.7	27.8	41.3
At −18°C	ASTM D-445	195	409	703	1150
Viscosity index		82	121	152	154
Pour point, °C	ASTM D-97	<−65	<−65	−45	−18
Flash point, °C	ASTM D-92	190	228	256	272
NOACK, % loss[a]	DIN 51581	55.7	11.5	3.5	2.3

[a] Volatility at 250°C.

The use of alternative (other than 1-decene) olefin streams as the starting olefin for PAO manufacture offers the opportunity to "tailor-make" products for niche markets [19]. Table 30 gives an indication of what happens when different linear α-olefins are reacted identically.

As mentioned earlier, decene was the raw material of choice for all the PAO producers because it gives products with the broadest temperature operating range. But for many applications, properties exhibited at one end of the temperature range may be more important than those at the other. For instance, a piece of industrial machinery that runs continuously at high temperature may have few, if any, low temperature requirements but may require a very stringent volatility or flash point specification. In such a case, a PAO based on 1-dodecene or 1-tetradecene may be more appropriate than 1-decene. Performance characteristics that can be enhanced by the appropriate choice of starting olefin and reaction conditions include volatility, pour point, viscosity index, low temperature viscosity, flash and fire points, thermal and oxidative stability, and biodegradability [115].

The development of new catalyst systems for the production of olefin oligomers having specific isomer distributions also holds the potential for the development of new PAO products with enhanced characteristics [116].

A new class of poly(α-olefin) fluids has been reported. These materials, referred to as HVI-PAO, have high viscosity indices and good pour points [117]. The HVI-PAO fluids derive their properties from being prepared using a chromium on silica catalyst system.

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APPENDIX: Typical Properties of Decene-Based PAOS

Table A1 Specific Heat and Thermal Conductivity

	Specific heat (cal/g/°C)	
	At 75°C	At 100°C
PAO 2	0.551	0.576
PAO 4	0.567	0.597
PAO 6	0.528	0.548
PAO 8	0.555	0.573
PAO 10	0.546	0.572
PAO 40	0.553	0.574
PAO 100	0.530	0.552

Test[a]	PAO 2	PAO 6	PAO 40
	Thermal conductivity [mW/(m · k)]		
	Equ. of line $137.60 - 0.0588T$	Equ. of line $149.20 - 0.0482T$	Equ. of line $164.10 - 0.0189T$
0.0°C	137.60	149.20	164.10
50.0°C	134.66	147.19	163.15
100.0°C	131.72	144.38	162.21
150.0°C	128.78	141.97	161.26
200.0°C	125.84	139.56	160.32
250.0°C	122.90	137.15	159.37
	Specific heat capacity [J/(g · k)]		
	Equ. of line $2.052 + 0.00377T$	Equ. of line $2.046 + 0.00370T$	Equ. of line $2.045 + 0.00352T$
0.0°C	2.052	2.046	2.045
50.0°C	2.241	2.231	2.221
100.0°C	2.429	2.416	2.397
150.0°C	2.618	2.601	2.573
200.0°C	2.806	2.786	2.749
250.0°C	2.995	2.971	2.925

[a] Differential scanning calorimetry under nitrogen gas (50 cm^3/min); open Al pan.

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Table A2 Physical Properties

Property	PAO 2	PAO 4	PAO 6	PAO 8	PAO 10	PAO 40	PAO 100	Test method
Color	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	ASTM D-1500
Kinematic viscosity, cSt								
At 200°C	0.73	1.31	1.75	2.06	2.35	—	—	ASTM D-445
At 150°C	1.05	1.90	2.65	3.26	3.94	12.9	29.0	ASTM D-445
At 125°C	1.35	2.61	3.77	4.88	5.82	16.6	50.0	ASTM D-445
At 100°C	1.80	3.90	5.90	7.80	9.60	40.0	100	ASTM D-445
At 40°C	5.54	16.8	31.0	45.8	62.9	395	1,250	ASTM D-445
At −18°C	62.0	341	901	1,605	2,770	40,200	203,000	ASTM D-445
At −40°C	310	2,460	7,890	18,160	32,650	—	—	ASTM D-445
Viscosity index	—	129	138	140	134	151	168	ASTM D-2270
Brookfield viscosity at −40°C, cP	—	2,100	6,950	16,920	—	—	—	—
Cold crank simulator at −25°C, cP	—	490	1,300	3,100	—	—	—	—
Pour point, °C	<−65	−70	−68	−63	−53	−34	−20	ASTM D-97
Flash point, °C	>155	215	235	252	264	272	288	ASTM D-92
Fire point, °C	—	250	268	286	300	310	320	ASTM D-92
NOACK volatility, wt % evap[a]	99	12	7.0	3.0	2.0	0.8	0.6	DIN 51581
Specific gravity at 15.6/15.6°C (60/60°F)	0.797	0.818	0.827	0.832	0.836	0.845	0.856	ASTM D-1298
Density at 15.6°C (60°F), lb/gal	6.653	6.81	6.89	6.93	6.97	7.04	7.13	—
Total acid number, mg KOH/g	—	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	ASTM D-974
Bromine number, g Br/100 g	0.5	0.2	0.2	0.3	0.4	—	—	IP-129
Moisture, ppm	50	11	13	13	19	—	—	ASTM D-1744
Molecular weight	287	437	529	596	632	1,400	2,000	GC (calc'd)
Differential scanning calorimetry								
Oxidation, onset temperature, °C	—	192	192	191	191	189	188	—
Energy, kJ/g	—	12.1	12.4	13.8	13.6	13.8	14.6	—
Aniline point, °C (°F)	—	116.7 (242)	129.6 (265)	123.3 (254)	132.2 (270)	153.3 (308)	154.4 (310)	ASTM D-611
Evaporative weight loss, %	—	11.8	4.6	3.3	1.6	—	—	ASTM D-972
Dielectric constant[b]	2.076	2.102	2.118	2.122	2.130	2.150	2.151	—
Vapor pressure, mmHg								
At 37.8°C (100°F)	—	—	<0.00047	0.00030	0.00010	—	—	—
At 93.3°C (200°F)	—	—	0.00101	0.00062	0.00050	—	—	—
At 148.9°C (300°F)	—	—	0.0019	0.0016	0.0017	—	—	—

[a] At 250°C, 1 hour.

[b] At 23°C, 1.0 and 1000 kHz.

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Table A3 Seal Compatibility

Elastomer	Tensile strength (% change)	Elongation (% change)	Volume (% change)	Hardness (change points)
		CCMC G5 Specification		
Fluoroelastomer RE1				
PAO 4	−4.5	−19.0	+1.0	−1.0
PAO 6	−1.2	−13.0	+0.6	0.0
PAO 8	−1.8	−19.0	+0.3	0.0
PAO 10	+1.8	−16.0	+0.1	0.0
Finished lubricant limits	−50/0	−60/0	0/+5	0/+5
Acrylate RE2				
PAO 4	−16.0	−33.0	−0.70	+3.0
PAO 6	−12.0	−30.0	−1.50	+4.0
PAO 8	−8.10	−32.0	−2.30	−2.4
PAO 10	−4.70	−27.0	−2.40	+5.0
Finished lubricant limits	−15/+10	−35/+10	−5/+5	−5/+5
Silicon RE3				
PAO 4	−19.00	−11.00	+32.50	−18.00
PAO 6	−09.60	−15.90	+18.00	−13.00
PAO 8	−04.20	−14.00	+13.30	−11.00
PAO 10	−04.10	−15.00	+10.90	−10.00
Nitrile RE4				
PAO 4	+11.00	−23.00	−01.20	+03.00
PAO 6	+13.00	−19.00	−01.90	+02.00
PAO 8	+11.00	−24.00	−02.20	+04.00
PAO 10	+11.00	−23.00	−02.30	+0.300
		Z. F. TE-02 MIL Specification		
FPM 8002: Viton				
PAO 8	+5.10	−15.00	+0.20	+2.00
PAO 10	+5.80	−14.00	0.00	+2.00
PAO 40	+4.30	−11.00	+0.20	+1.00
NBR SRE 28: Nitrile				
PAO 8	+1.30	−26.00	−0.90	+2.00
PAO 10	−2.20	−29.00	−1.20	+2.00
PAO 40	0.00	−29.00	−2.00	+1.00
		Mercedes Benz 235.0/1 Specification		
FPM SRE 281: Viton				
PAO 8	+2.20	−1.00	+0.10	−1.00
PAO 10	−2.20	−4.20	+0.10	+1.00
PAO 40	−12.00	−5.70	+0.20	−1.00
NBR SRE34: Nitrile				
PAO 8	+8.80	−19.00	−2.00	+3.00
PAO 10	+5.00	−24.00	−2.10	+3.00
PAO 40	+2.90	−29.00	−2.10	+4.00

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Table A4 Simulated Distillation, ASTM D-2887

	Fluid temperatures (°C)				
Amount distilled (%)	PAO 2	PAO 4	PAO 6	PAO 8	PAO 10
1	185	369	369	344	424
5	204	391	391	402	461
10	210	402	402	432	473
20	217	412	412	468	479
50	229	422	476	491	492
90	244	468	525	537	537
95	339	476	525	548	542
99	350	518	560	560	547

Table A5 Typical Composition

	Normal area (%)[a] for				
Composition	PAO 2	PAO 4	PAO 6	PAO 8	PAO 10
Dimer	99.0	0.6	0.1	—	0.1
Trimer	1.0	84.4	33.9	6.0	1.1
Tetramer	—	14.5	43.5	55.7	42.5
Pentamer	—	0.5	17.4	27.2	32.3
Hexamer	—	—	3.8	7.0	11.8
Heptamer	—	—	1.3	4.1	12.2

[a] As determined by gas chromatography.

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Table A6 Typical Properties of Non-Decene-Based PAOs

Physical Properties	2.5 cSt	5 cSt	7 cSt	9 cSt	Test method
Color	+30	+30	+30	+30	ASTM D-158
Kinematic viscosity, cSt					
At 100°C	2.4	5.0	7.0	8.8	
At 40°C	8.3	24.2	38.4	55.9	ASTM D-445
At −40°C	1,811	4,400	11,500	—	
Viscosity index	—	145	145	143	ASTM D-2270
Pour point, °C	−52	−50	−43	−42	ASTM D-97
Flash point, °C[a]	188	246	260	271	ASTM D-92
Fire point, °C[a]	210	278	290	304	ASTM D-92
NOACK volatility, wt %	—	5.5	2.3	1.5	DIN 51581
Specific gravity	0.8074	0.8235	0.8315	0.8346	ASTM D-1298
Density, lbs/gal @ 15.6°C	8.74	8.87	6.92	6.98	—
Total acid number, mg KOH/g	<0.03	<0.03	<0.03	<0.03	ASTM D-974
Appearance	Clear and bright	Clear and bright	Clear and bright	Clear and bright	ASTM D-4176
Odor	No foreign odor	No foreign odor	No foreign odor	No foreign odor	ASTM D-1288

[a] Cleveland open cup method.
Source: Chevron PAO products bulletin.

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